Part I. Measurement of helium production by radio-active elements. Part II. Studies on isotopic exchange in heterogeneous systems.

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Tuck, Dennis George (1956) *Part I. Measurement of helium production by radio-active elements. Part II. Studies on isotopic exchange in heterogeneous systems.*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/9144/

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THESIS

presented in candidature for the degree of

DOCTOR OF PHILOSOPHY

of the University of Durham

by

Dennis George Tuck, B.Sc., (Dunelm).

Being in two parts, entitled

PART I. MEASUREMENT OF HELIUM PRODUCTION BY RADIO-ACTIVE ELEMENTS.

PART II. STUDIES ON ISOTOPIC EXCHANGE IN HETEROGENEOUS SYSTEMS.

FOREWORD

Part I of this thesis is an account of work carried out in the Londonderry Laboratory for Radiochemistry, University of Durham during the period 1949-1952, under the supervision (from 1949 until 1951) of Dr. K. F. Chackett, B.Sc., Ph.D.

Part II describes work carried out in the academic year 1952-1953 in the Laboratoire Curie, Institut du Radium, Paris under the direction of Dr. M. Haissinsky.

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SUMMARY

In the opening chapter of Part I of this thesis, the reasons necessitating a redetermination of the specific alpha-activity of radium are discussed in relation to the question of radioactive standards. Previous values are reviewed and the advantages of the helium method emphasised.

The apparatus and experimental methods used in the estimation of microquantities of helium (of the order of 10^{-6} cc.) are fully described. Details are given of the standardisation of a new calibrating system. In an appendix to Part I, a theoretical discussion of the behaviour of the Pirani gauge, as used in this apparatus, is presented.

The equations governing the rate of formation of helium from radium and its daughter products are deduced. Preliminary measurements of the specific alpha-activity of radium, using a solution of radium bromide, gave results in satisfactory agreement with those of earlier workers. After a lapse of some time for repair of the helium apparatus, helium yields with an accurately calibrated solution of radium chloride were excessively high. This was shown to be due to the formation of a highly adsorbent silicaceous deposit in the solution; by holding back radon in the solution, the premises of the equations used are rendered invalid. The formation of this deposit is discussed later, and experimental work on its origin described. It was later shown that helium yields from radium solutions in soda-glass vessels are initially reproducible, but begin to rise after a comparatively short period of time. The initial results could not be used to deduce an accurate value for the specific alpha-activity of radium, since the radium content of the solution was not known sufficiently accurately.

A further series of experiments were carried out using a solid source of radium, releasing helium by fluxing under vacuum. Development work on this method is described. Because of apparatus troubles, accurate results were not obtained, but reasons for preferring this technique are given with other suggestions for future work. The question of the loss of alpha-particles into the walls of the vessel containing such a solid source is considered in a short mathematical discussion.

In the introductory chapter to Part II, the nature and the kinetics of isotopic exchange reactions are discussed, with particular reference to the possible rate-controlling processes in such reactions in heterogeneous systems. After a description of the techniques used in experiments on the selenium-polyselenide ion exchange, it is shown that the allotropic transformation (red Se ⟶ black Se) taking place in the presence of a solution of polyselenide ions accounts for the anomalous temperature effect noted in previous work. Surface recrystallisation was identified as the rate-controlling process in the exchange between black selenium and polyselenide ions; this was confirmed by electron diffraction photographs. The results are compared with those of other workers and the limitations of the data obtainable from heteogeneous isotopic exchange reactions discussed. Direct measurements of the self-diffusion coefficient of metallic selenium are described; volume and grain-boundary diffusion were observed. The results confirm the conclusions drawn from the exchange experiments.

Work on the exchange reaction between liquid mercury and mercurous ions was initiated in an attempt to explain the contradictory values for the self-diffusion coefficient of mercury obtained from earlier exchange experiments

and from direct measurements. The present work confirms the main results of both series of experiments. In a discussion of the rate-controlling process in the mercury-mercurous ion exchange, it is shown that no slow step can occur in the aqueous phase because of the rapid dismutation of the mercurous ion. It is proposed that the significantly slow step is the slow diffusion of a mercury atom across the interface into a vacancy in the water structure. Work on amalgam-solution exchange reactions and experiments on interfacial transfer in oil-water systems are in accordance with the mechanism proposed.

PART I

MEASUREMENT OF HELIUM PRODUCTION BY RADIOACTIVE ELEMENTS

CHAPTER I. THE SPECIFIC α-ACTIVITY OF RADIUM

Ia. Radioactive Standards

From the earliest days of radioactivity, the need for accurate standards has been recognised, since without them, the quantitative comparison of results from different laboratories lacked reliable foundation. The first international standard was prepared by Mme. Curie in 1911, using a purified sample of radium chloride; at that time radium* was the radio-element most easily available in good purity. By comparison of the radiations from this standard with those from an unknown source, the activity of the unknown could be expressed in terms of a weight of radium. For the measurement of radon the unit used was the amount of radon in radioactive equilibrium with 1 gm. of radium. This unit of activity became known as the "curie".

The comparison of sources with the standard always involved measurements of ionization current or of the disintegration rate and since these were easier to determine than the weight of radium in a source, it became customary to base the curie directly on the number of α-particles emitted in unit time. For this purpose, the value of 3.7×10^{10} α-particles per second per gram was accepted as the best value for the activity of radium. Later, this practice was extended to radio-elements other than members of the radium disintegration series, by comparing their rate of particle emission with the above value, so that the curie became the unit of strength for any radioactive source.

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*In this thesis the term radium refers to the nuclide Ra^{226}.

Despite the wide use of the curie in this sense the definition was still based on the weight of a radium preparation; furthermore, the disintegration rate of radium itself was still comparatively uncertain.[1] The disadvantages of this system were underlined by a redetermination of the specific α-activity of radium, giving a value of $3.61 \times 10^{10} \alpha.\mathrm{sec.}^{-1}\ \mathrm{gm.}^{-1}$. After some discussion (which included the recommendation of the acceptance of this value by the International Union of Physics[2]), the newly established Joint Commission on Standards, Units and Constants of Radioactivity[3], redefined the curie in the following manner:-

"The curie is a unit of radioactivity defined as the quantity of any radioactive nuclide in which the number of disintegrations per second is 3.700×10^{10}".

This new definition severs the former basis of the curie upon the activity of a weight of radium; at the same time, the figure 3.700×10^{10} was chosen to keep the new definition as close as possible to the old one.

The international radium standards, at present in Paris and Vienna, replaced the original preparation of Mme. Curie in 1934. These primary standards, and the various national secondary standards are still the basis of γ-ray comparisons of sources, such as the measurement of radon for therapeutic use. Such standards cannot be expressed in terms of the new definition of the curie until the activity of radium itself can be expressed in curies. The correction factor implied in such a re-definition will clearly be close to unity.

Ib. The Specific Activity of Radium

It is unfortunate, in view of the special position which radium occupies in the field of radioactive standardization, that the measurement of its specific activity is attended with special difficulties. The half life is too long to allow accurate decay measurements, whilst the presence of significant α- and γ-activity from the short-lived daughter elements interferes with both direct and indirect measurement of the α-emission from radium itself. In spite of the importance of this constant and the many determinations which have been reported, the accuracy with which it is known is comparatively low. Indeed, St. Meyer[4] has expressed the opinion that an accuracy better than 1% cannot be expected. Table 1 illustrates the wide diversity of results to be found in the literature; the values have been recalculated in some cases, by Kohman[5] using modern data (for the electronic charge, for example).

TABLE 1

Published values for the specific α-activity of radium
$10^{10}\ \alpha.\text{sec.}^{-1}\ \text{gm.}^{-1}$

Growth rate from ionium	2.98	3.53	3.47	3.47		
Counting methods	3.4	3.72	3.7	3.40	3.66	3.61
Electrical charge measurements	3.22	3.15	3.50	3.48	3.68	3.65
Evolution of heat	3.75	3.72	3.63	3.68		
Helium measurements	2.9	3.88	3.70	3.33	3.67	

The reliability of these figures obviously varies widely. Kohman has pointed out that many of the determinations depend ultimately on the comparison of the radium source used with a standard by γ-ray measurements. This process may have an error of 0.5% or more due to geometrical and other errors; such errors of course are carried through to the final result. Other experiments have used the daughter elements rather than radium itself and here again systematic errors may be introduced. Collected under broad headings as in the table, the groups show little or no family affinity. The best internal correlation appears in the results obtained by measurement of the heat generated in α-, β- and γ- emission, although in such experiments corrections must be applied for incomplete absorption of γ-radiation in the calorimeter. Many of the earlier counting experiments suffered from the relative crudity of the apparatus then available, which also necessitated considerable dilution of the source. Measurement of electric charge on the particles involves rather uncertain conversion factors. The values obtained by measuring the rate of the process $\mathrm{Io} \xrightarrow{\alpha} \mathrm{Ra} \xrightarrow{\alpha} \mathrm{Rn}$ are consistently below the average. This has been attributed to the use of minerals which were too young for the attainment of true radioactive equilibrium, or which were not intact enough for the equilibrium to have been preserved. In general, then, the large errors which may exist in the values quoted above are understandable.

Ic. The Helium Method of α-particle Measurement

Because of the difficulties implicit in direct counting of the α-particles from radium, methods which effectively integrate this α-flux have many advantages. One such method which detects specifically α-

particles only is the measurement of the helium formed in the decay of a radium source. The results obtained by this technique in previous experiments are collectively no better than for any other group (Table 1), but it must be emphasised in this connection that the first four determinations were carried out before 1910, at which time such techniques were in their infancy.

At the present time, the apparatus and techniques for the determination of quantities of helium of the order of 10^{-6} cc. are highly developed. Details will be discussed in the following chapter; in evidence of the accuracy attainable, one can point to the published results[6] on the composition of ground-level and stratospheric air. Furthermore, the results obtained by Gunther[7] in 1939 show excellent agreement (see later). The quantity of radium needed to generate suitable volumes of helium is in the order of a few milligram which can be weighed directly, thereby avoiding one of the main uncertainties in previous determinations. In general, then, it is suggested that the helium method provides a direct and accurate method for the measurement of the specific α-activity of radium, free from any unjustifiable assumptions.

Id. The Experiments of Kohman, Ames and Sedlet

Since the work of Kohman and his collaborators[5] is the most recent determination of the specific activity and has not been published in any journal, a short description of the method will be given. Commercial $RaBr_2$ containing a negligible amount of $MsTh_1$ (Ra^{228}) was freed from barium by a series of fractional crystallisations from hydrochloric acid. Weighed quantities of this pure $RaCl_2$ were dissolved in $HClO_4$ and refluxed with the quartz weighing vessel until the activity of the latter was negligible. These solutions were made up to a known volume, aliquots of each taken for counting and evaporated onto platinum counting trays which were weighed before and after the aliquoting. To prevent liquid running to the edges of the tray during evaporation, a temperature gradient was maintained from the edge to the centre. Finally the plate was flamed to drive out radon and counted, the deposit being later examined with a low-power microscope to ensure that only uniformly and thinly deposited samples were considered for the final result. The counter used was a parallel plate ionisation chamber with a scaling circuit biased against weaker pulses due to β- and γ-emission. The final value was $3.608 \pm 0.028 \times 10^{10}$ α/sec./gm. from two series of experiments.

The difference between this result and the accepted (average) value is difficult to understand. The difficulties involved in counting activities of such an order must be very great, but Kohman and his collaborators have clearly taken great precautions on this point. A series of experiments of great value would be to count directly the α-particles from radium alone, using a pulse-analyser arrangement. In this way any uncertainties about corrections for activities of the active deposit could be overcome.

Ie. The Experiments of Dewar

The first recorded attempt to measure directly the amount of helium produced by radium was that of Dewar[8] in 1908. A vacuum apparatus which could be evacuated to a high degree by the use of charcoal cooled in liquid air was employed, with 70 mgm. of purified radium chloride. The gas was driven out of this by heating, and the volume not adsorbed by the cooled charcoal measured in a calibrated MacLeod gauge; precautions were taken to ensure that the only gas measured was helium. The final result given is 0.37 cubic mm. of helium per gram of radium per day. By modern standards Dewar's method is open to much criticism, but in view of the experimental difficulties involved, his result is remarkably close to the accepted value. This is especially the case when a correction, later noted by Dewar, is made, giving a corrected value of 0.499 cubic mm. per day per gram of radium. (The correction was due to an error in the measurement of the volume of the apparatus).

A later series of experiments by the same author[9] using the same source of radium, involved measuring the helium accumulated after nine months by similar techniques. This gave a value of 0.463 cubic mm. per day per gram of radium. Dewar points out that in his opinion, the true value may lie between these two results, in view of the different conditions of the experiments. The helium production is, of course, that for radium in equilibrium with its short-lived daughter products. The values for the specific α-activity of radium obtained from Dewar's results are 3.88 and 3.70 α/sec./gm.; the agreement with later determinations is good.

If. The Experiments of Boltwood and Rutherford

A series of experiments on the production of helium by α-active natural radio-elements was carried out by these authors[10] in 1910. Besides measuring the amount of helium from radium, they were able to show the agreement between the theoretical and experimental rate of generation of helium for polonium and radon, and to detect its formation from radium-D (i.e. from the daughter polonium).

In their measurement of the helium produced by radium, a source whose γ-activity was equivalent to 192 mgm. of radium was used. The long-lived daughter elements were removed and the resultant (dry) salt was placed in a platinum capsule itself placed in a Jena glass vessel which could be opened under vacuum. Before heating the salt to drive out the generated helium, the tube was examined to determine the proportion of radon escaping from the solid and diffusing into the upper portion of the tube; if this amount was high, the α-particles from the active deposit might be to some extent lost irrecoverably into the walls. The γ-activity of the upper part of the tube, with the lower part covered with a thick block, was too small to be detected (less than 1% would have been easily observed), so that the escape of radon from such a solid is negligible. The question of the loss of α-particles into the walls from the solid itself is discussed later.

After heating the salt, a further series of gamma measurements showed that the radon had been completely separated from the solid by the heating process. It therefore was assumed that helium was also completely removed. Periods for accumulation of 83 and 132 days were used, and the measurement of helium carried out in an accurately calibrated MacLeod gauge system. The final value was 0.156 $cm.^3$ per year per gram, in good agreement with the figure of 0.158 $cm.^3$ calculated from the results of the counting experiments of Rutherford and Geiger[11]. The daily rate for radium in equilibrium with its short-lived daughter elements is therefore 0.428 $mm.^3$ per gram. It was found that the radium salt used by Dewar was equivalent to 72 mgm. of radium by the standard used by Boltwood and

Rutherford, so that according to the latter authors the annual rate of helium production in Dewar's experiments should be 164 instead of 169 mm.^{3} per gram; the agreement is quite good. It is interesting to note that one of the main conclusions of these experiments was that the agreement between theoretical and experimental rate of helium production proved the atomic theory. Already, however, one realised the intrinsic value of the helium method inasmuch as it is free from assumptions about fundamental constants (such as the charge on the electron).

Ig. <u>The Experiments of Gunther</u>

The most recent determination of the specific α-activity of radium by the helium method is that of Gunther[7], who published simultaneously the results of similar experiments with uranium. In the radium work, a source of radium chloride was freed from polonium and radium-D by the usual radiochemical methods, and the purified salt precipitated as carbonate after addition of a small amount of barium as carrier. The γ-activity of the salt was compared with a standard, and showed the presence of 16.4 mg. of radium. The salt was dissolved and the solution placed in a vessel of the type shown in Figure 1. By completely filling the larger (500 ml.) flask with solution, the existence of radon in the gas phase during accumulation of helium was prevented, so that there could be no loss of helium due to α-particles from the active deposit entering the walls.

The measurement of the helium generated was carried out by the analytical techniques then available; the results are given in Table 2.

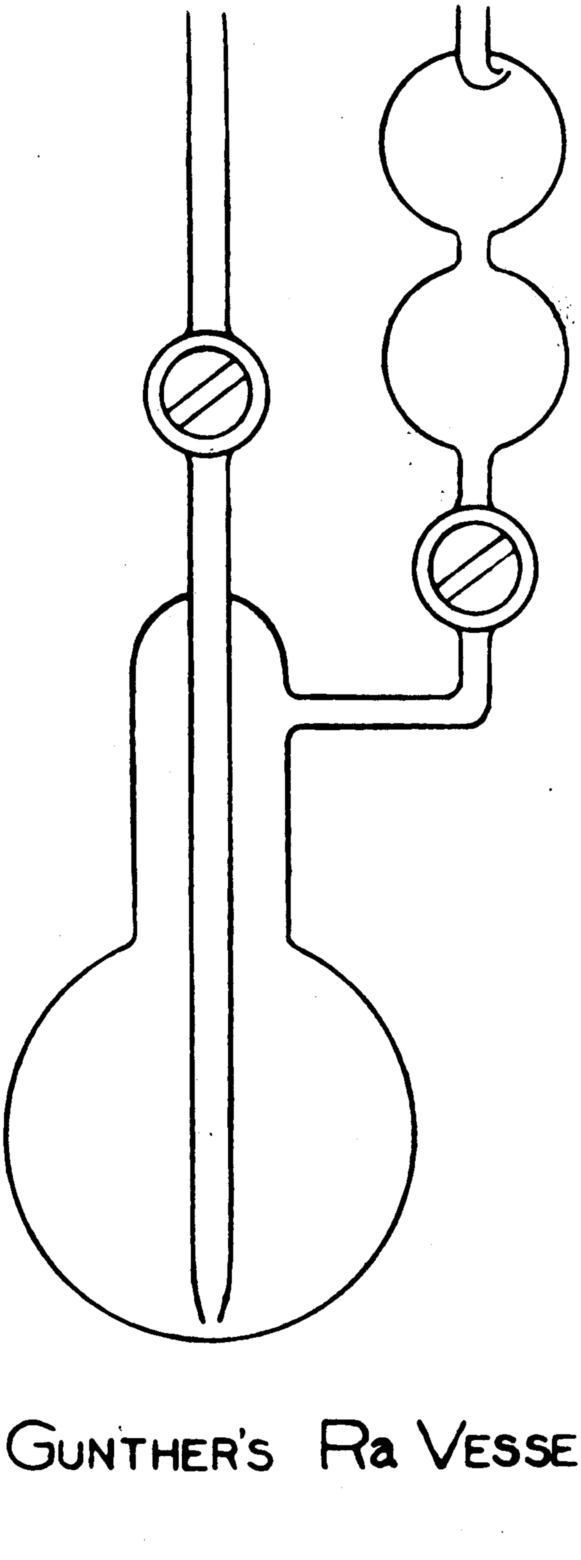


FIGURE 1. GUNTHER'S Ra VESSEL

TABLE 2			
	Time (hrs.)	Vol. of He found $1\bar{0}^{6}$ cc.	He per mg. Ra hr.$^{-1}$ $1\bar{0}^{9}$ cc.
1	92	13.6	4.87
2	119	19.8	4.89
3	120.5	19.9	4.93
4	150	26.8	4.93
	Average value 4.89 ± 0.03 x 10^{-9} cc. He hr.$^{-1}$		

From this average value, one calculates the specific α-activity of radium as 3.67 x 10^{10} α sec.$^{-1}$ gm.$^{-1}$. The results show good internal consistency although of course the absolute value of the specific activity depends on the accuracy with which the strength of the radium source was estimated.

CHAPTER II. DESCRIPTION AND USE OF THE HELIUM APPARATUS

IIa. Historical Note

The existence of a new element in the sun's atmosphere was first observed spectroscopically by Lockyer[12] in 1869, but not until 1895 was the presence in terrestial minerals of the element helium demonstrated by Ramsay[13]. The first identification as a constituent of the earth's atmosphere was by Kayser[14]; its occurrence in practically all rocks was demonstrated by Strutt[15]. The significance of the helium nucleus in the study of radioactivity was soon realised; it is of particular interest to the subject of this thesis to note the first experimental proof that helium could be obtained from radium salts and from radium emanation, by Ramsay and Soddy[16]. The identity of the helium nucleus and the α-particle was suggested[17] and ultimately confirmed by Rutherford[18].

The first papers in the series of 'Helium Researches' of Paneth and his collaborators were published in 1928. In the earlier work[19], spectroscopic determination of helium (and neon) was used to measure, for example, the amount of helium formed by 0.1 mc. of thorium active deposit. Other work[20, 21] included the determination of the age of iron meteorites and the helium content of certain European natural gases. In 1930, the Pirani gauge was first used for volumetric measurement of helium and neon[22]. Following further age determinations by the helium method[23], certain nuclear reactions were investigated[24], such as the production of helium following the (γ, n) reaction on Be^9. In the years before the war, a long series of measurements[25] was performed on the helium, neon and argon content of the earth's atmosphere. Post-war researches[26] extended these researches to samples taken in stratospheric rocket flights; above 60 Km. height, some diffusive separation of the lighter elements appears to occur.

Other workers in the helium field have published work on such topics as the rate of helium diffusion through glass[27], the half-life of α-emitting elements[7], and the separation of helium and neon[28]. In general, such work has been by former collaborators of Paneth.

IIb. General Description

The apparatus employed for helium determinations in the present work bears a direct relationship to that used by earlier workers. It consists essentially of an arrangement for quantitative transfer of helium from the generating medium into the main apparatus, using oxygen as a carrier gas; a circulating system for the catalytic oxidation of hydrogen; and a fractionating column for purification of helium by an adsorption method before final measurement in a Pirani gauge system; a pipetting system supplies known volumes of pure gas for calibrating these gauges. An apparatus for purifying and storing oxygen is also provided. Soda glass is used throughout, since pyrex is permeable to helium, even at room temperature[29].

The micro-quantities of gas involved necessitate the whole apparatus being evacuated to a very low pressure. The high vacuum pumping system consists of a rotary oil pump backing two mercury diffusion pumps in series; liquid nitrogen traps prevent diffusion of mercury vapour into the main vacuum lines, and diffusion of oil and mercury vapour between backing and diffusion pumps. The pressure in the main vacuum can be measured with a MacLeod gauge. Apiezon grease 'N' was used as a lubricant for all taps; ground joints were sealed with Apiezon grease 'M', Everett's wax No. 1, or Apiezon wax 'W', depending on their precise function in the apparatus. A pressure of the order of 10^{-6} mm. was easily obtained in this system.

IIc. Collection of Helium from a Source

In order to make possible the manipulation of micro-quantities of helium, purified oxygen is used as a carrier gas. The admixture of this gas is made in the vessel in which helium is being released from its source: particular techniques will be described later. A diagram of the experimental arrangement which leads into the circulating system through a special ventil is shown in Figure 2. Helium is released into the evacuated space defined by the tap 2 and oxygen is added via tap 1, from a non-return valve (see section IIi). When the pressure recorded by the manometer reaches about 10 cm. the tap 1 is closed and tap 2 opened. By cooling a suitable charcoal tube in the circulating system and using the ventil as a non-return valve (see section 6), the oxygen-helium mixture passes across. The amount remaining clearly depends on the height of mercury in the ventil; this is generally of the order of 5-10 per cent of the total. This operation is carried out six times, which ensures quantitative transfer of helium to the circulating system, since back-diffusion is prevented by the non-return valve.

The diagram actually shows in position the type of blank vessel used when the purity of the oxygen supply is being checked.

IId. The Circulating System

The gases which pass through the ventil are an excess of oxygen, the helium which is to be measured and small amounts of hydrogen, water vapour etc. (depending on the particular experiment being carried out). The ventil D (Figure 3) was designed to allow quantities of gas to pass freely without the

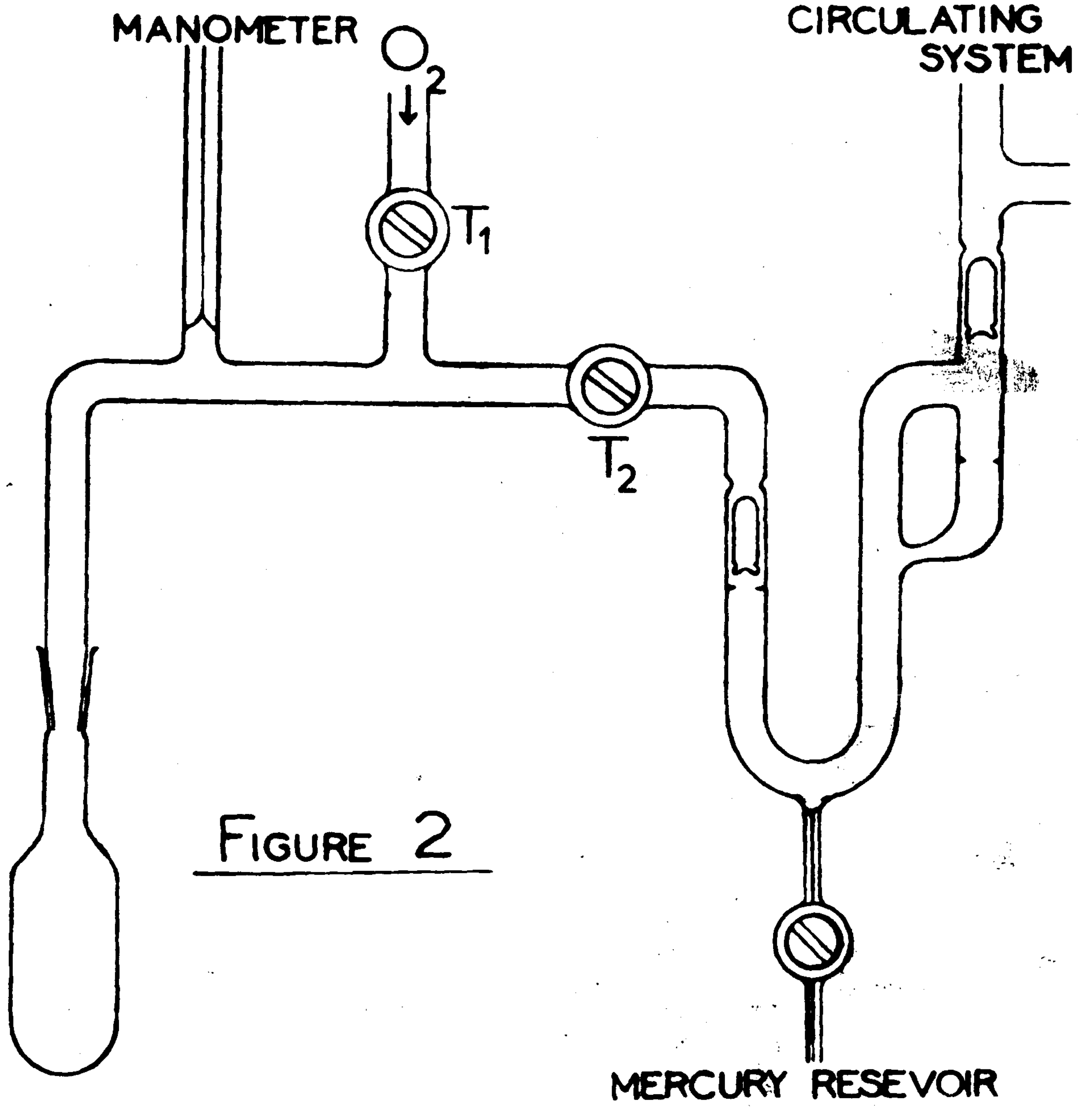


FIGURE 2

danger of the float being jammed against its seat by the gas pressure; when the mercury no longer supports the float, the latter remains in the by-passed limb. During the passage of gas into the circulating system, the mercury level is adjusted to form a non-return valve whilst the tap K is, of course, closed, and J remains open. The charcoal tube I is cooled with liquid nitrogen throughout this process and thus a vacuum is maintained in the circulating system. After flushing out the radium-containing vessel six times with oxygen, the mercury in the ventil D is raised so as to form a completely closed system. The liquid nitrogen is then removed from the charcoal tube and the gases allowed to desorb and reach room temperature.

The mixture of gases is next circulated over heated palladium to oxidise any hydrogen present. The palladium furnace G consists of a coiled coil of blackened palladium tape in an electrically heated platinum tube. In any experiment with the solid source of radium, the only hydrogen present is that which may have desorbed from the walls of the steel furnace, but when a solution is used, much larger quantities of electrolytic hydrogen are found, along with some water vapour. In this latter case the circulating process is carried on for about twenty minutes; the pressure generally falls by about half a centimetre in the first few minutes, due to the formation of water. During experiments on the solid source, circulation need only be carried on for about five minutes. The water formed is frozen out in the trap H which is immersed in liquid nitrogen. The piston of the circulating pump F is a glass tube containing an iron core working in a close fitting outer tube against two ground ball valves. This piston is controlled by a solenoid which is activated by a make-and-break regulator, which may be set to operate at any desired frequency.

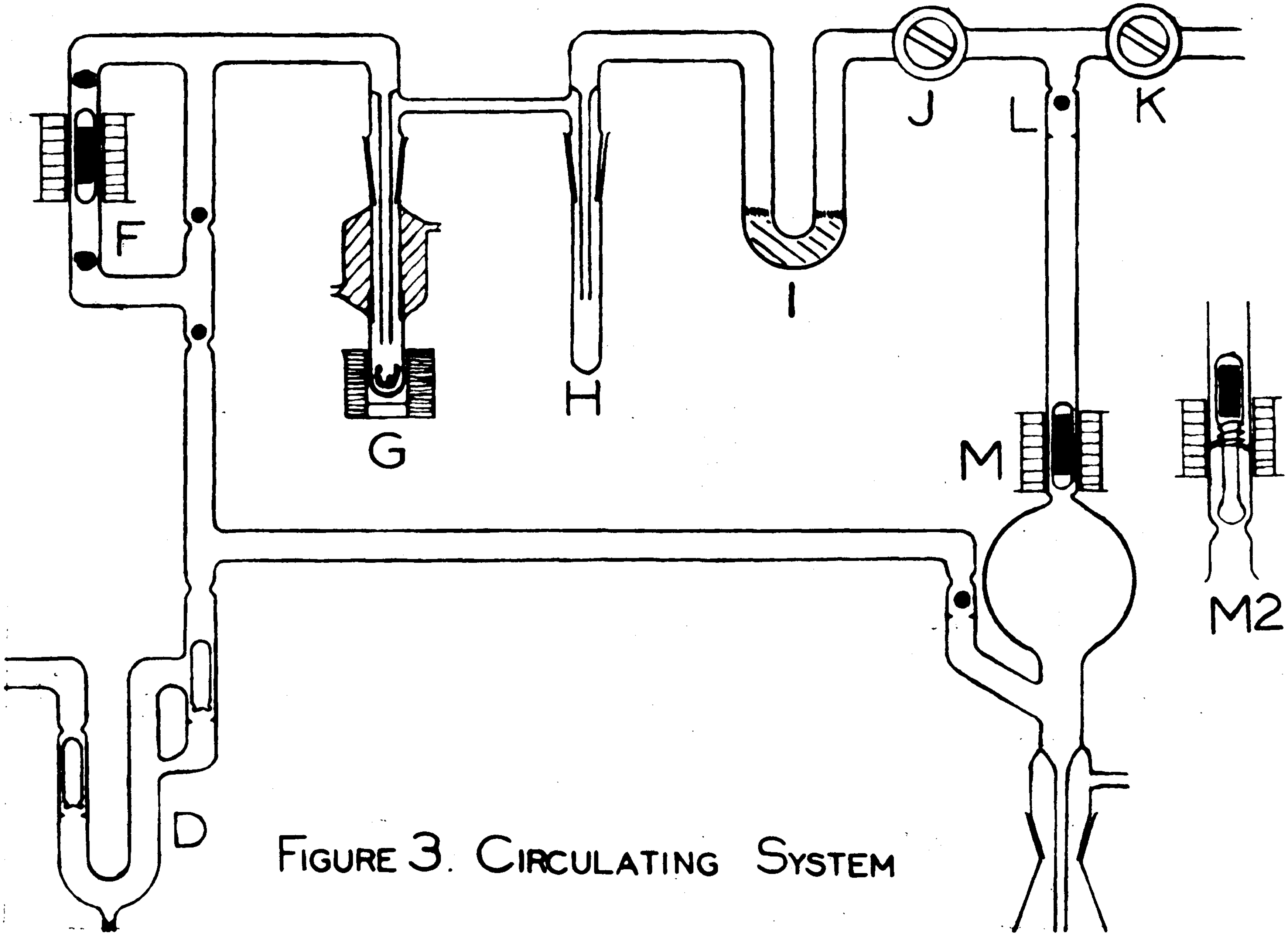


FIGURE 3. CIRCULATING SYSTEM

After the oxidation has been completed, the only gases remaining are an excess of oxygen and the helium to be measured (and any neon resulting from a leakage of air). The palladium furnace is switched off, and the tap J closed, and on opening K to the liquid-nitrogen cooled first charcoal U-tube of the fractionating column, most of the gases pass over. The remainder is pumped onto the charcoal by means of the Töpler pump, using the valve M to prevent back-diffusion of helium which is not absorbed by the charcoal. After six strokes of the Töpler pump, the mercury level is finally raised to the ball valve at L, thus reducing the dead space before the fractionating column to a minimum.

The original valve at M was such that it was necessary to pass current through the solenoid to raise the valve throughout the whole time of circulating. This caused considerable heat to be developed, which is clearly undesirable since glass is much more permeable to helium when hot than at room temperature. It was accordingly replaced by a valve M2 which was normally maintained open by a tungsten spring, and closed by the activation of the solenoid during operation of the Töpler pump; this proved quite satisfactory.

IIe. The Fractionating Column

Purification of the gases in the circulating system results in a mixture of oxygen, helium and possibly neon being passed into the fractionating column. This removes oxygen in the first stage and then separates helium and neon by fractional adsorption (and desorption) on charcoal cooled in liquid nitrogen. A comprehensive treatment of the theory and mode of operation of such a column has been given by Gluckauf[30].

The distribution of a gas between an adsorbent and the gas phase has been shown to be dependent upon the amount of adsorbent, the volume of the gas space, the temperature of the adsorbent and the adsorption coefficient of the particular gas. For a mixture of two gases of adsorption coefficients α and β, in a volume V ccs. above S gm. of adsorbent, it has been found that optimum separation requires the two conditions:

i. $V/S = \alpha/\beta$

ii. $a + b = 1$ where $a = \dfrac{1}{1 + \alpha S/V}$

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

From these relationships one can calculate the experimental conditions necessary to construct a system of adsorption units to form an efficient fractionating column. The column used in this work was designed to have twelve units, with S = 2.5 gm. (of activated charcoal) and V = 80 ccs.

A diagram of the system is shown in Figure 4. Initially, the whole column is evacuated and the charcoals warmed to about 150°C. under vacuum and allowed to cool before closing the relevant stopcocks. The mercury is then raised to level 'a' in the front bulb and level 'b' in the back series. Following the operations described in the previous section, oxygen is wholly adsorbed in the first charcoal tube C_1, whilst helium and neon will be present in the gas phase. By means of suitable valves to the atmosphere and to the secondary vacuum line, mercury is lowered to below the side arm entry (level 'b'), whereupon the inert gases distribute between the charcoal and the gas

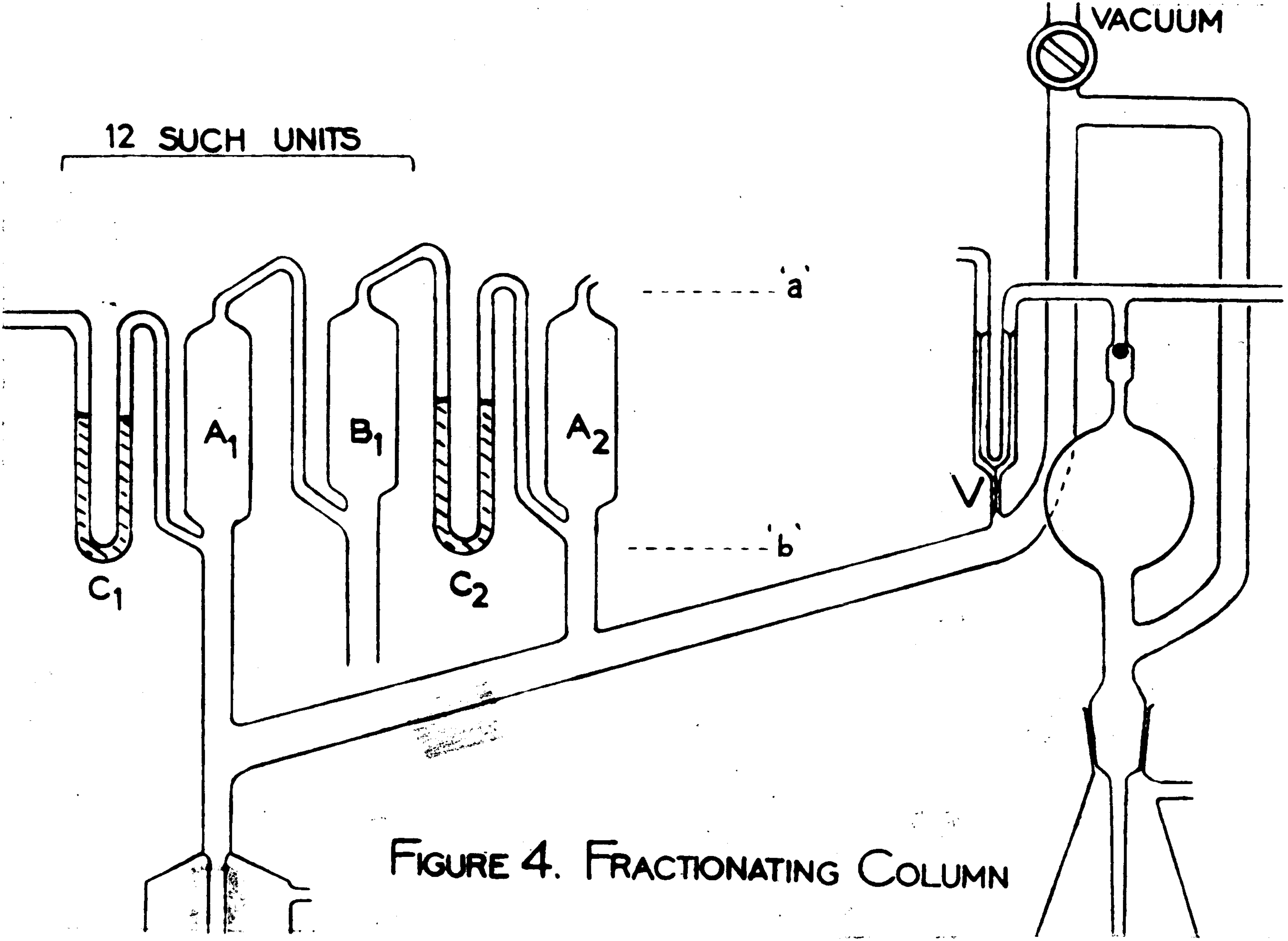


FIGURE 4. FRACTIONATING COLUMN

space. By raising the mercury in the front series of bulbs to 'a' and lowering that in the rear part of the column, the gas is transferred from A to B. This is followed by raising the mercury in the rear and lowering it at the front, whereby the gas is transferred to the second charcoal tube C_2. Such a transfer of gas from one charcoal tube to the next constitutes a single operation. Clearly, the bulbs function alternately as Töpler pumps and as equilibration spaces above the charcoals. One large Töpler pump is situated at the end of the fractionating column: gas leaving the twelfth unit is collected in this before being pumped into the Pirani gauge.

After twelve operations, helium should have reached the last unit without having passed into the Töpler bulb and the Pirani gauges are used to check that no gas has leaked into the system during this period. During the second twelve operations the bulk of the helium passes through and is collected and measured. The next operation is performed singly, in order to collect the helium retained in bulb B_{12}, which is retained when the ventil V is closed. Small, but not negligible amounts of helium are left in the column with the total neon which passes more slowly and is subsequently collected and measured. In order to speed up this process, the liquid nitrogen coolant baths are removed when the last amounts of helium have passed (except on C_1, where it is half-lowered in order to retain the oxygen carrier gas.

During the period of this work certain slight changes were made in the column and on each occasion a check was made to ensure that the distribution characteristics had not changed. Instead of constructing graphs of deflection against number of operations, as in Gluckauf's original paper, it was felt that a clearer picture could be obtained from a type of integral graph. Certain

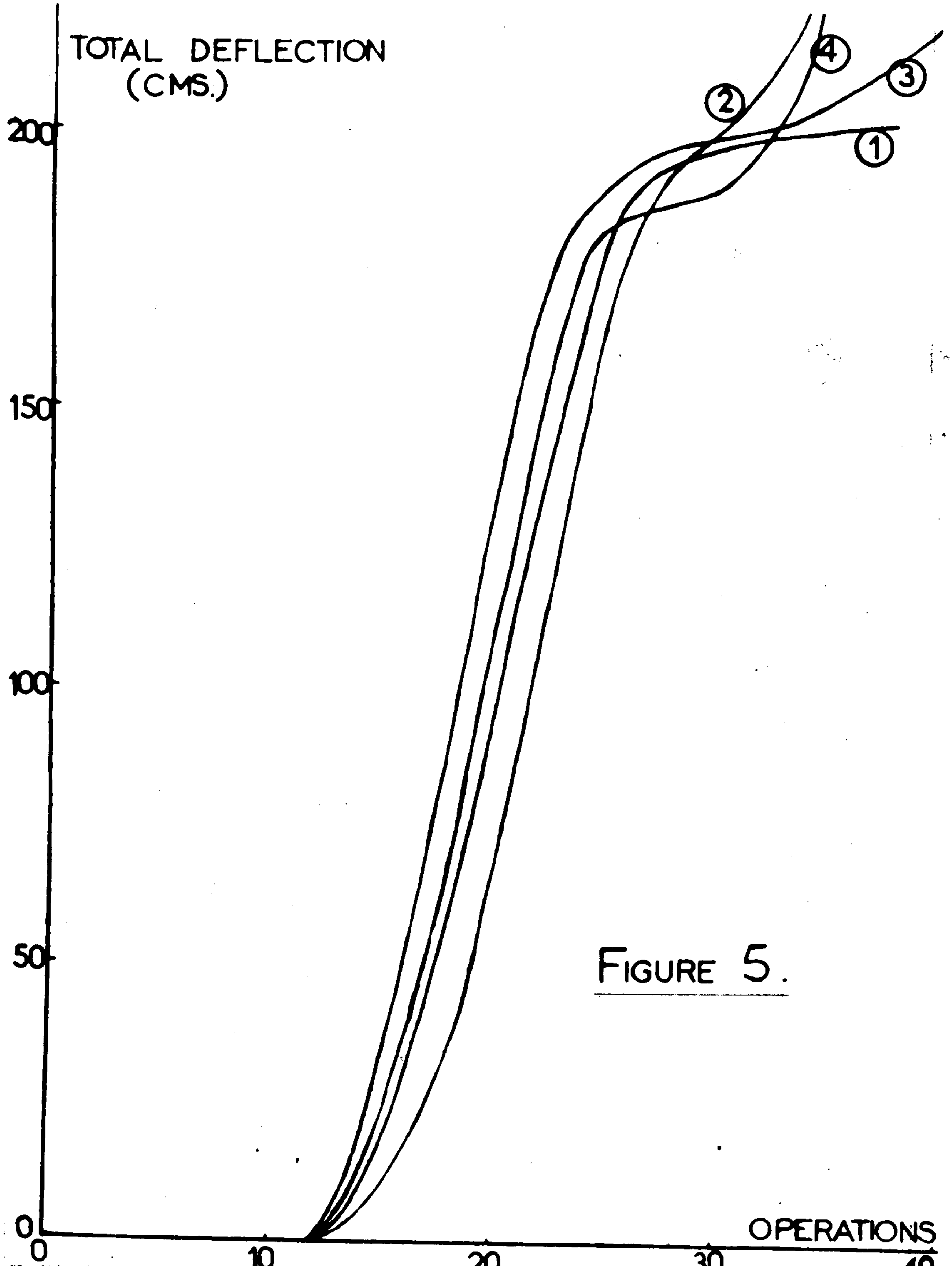

TOTAL DEFLECTION
(CMS.)
200
150
100
50
0
0
10
20
30
40
OPERATIONS
①
②
③
④

FIGURE 5.

examples are shwon in Figure 5; curve (1) shows the behaviour of pure helium in the column, (2) the normal type of separation curve for the helium and neon and (3) the effect of not removing the liquid nitrogen coolants from the charcoal tubes after elution of the helium; the neon is seen to come through much more slowly. Curve (4) shows the improved fractionation obtained after slightly changing the amounts of charcoal in each tube: presumably the original charcoal has been subject to some ageing effect. The distances separating the lower portions of these curves have been slightly exaggerated for the sake of clarity.

IIf. The Pirani Gauges

In order to measure accurately the micro-quantities of gas involved in this type of work, extremely sensitive Pirani gauges were used. In the early stages, a design due to Dr. W. J. Arrol was employed (see Figure 6A). A pair of these gauges **form** two arms of a Wheatstone network in conjunction with a resistance box and a moving coil galvanometer whose sensitivity can be varied. A potential of one volt is applied across the network since early work showed that in this region a plateau exists in the voltage-sensitivity graph: the implications of this are discussed later. Initially, the gauges are prepared for use by baking out the small pieces of charcoal with a small flame and then immersing the whole tube in hot water for half-an-hour whilst pumping on the gauges. This serves to drive off any mercury condensed on the filament. Gold "shavings" prevent mercury vapour attacking the filament or the soft-soldered joints during operation of the gauge. After allowing the gauges to cool down to room temperature, both gauges are closed and immersed in liquid nitrogen so that only the upper few inches of the gauge are

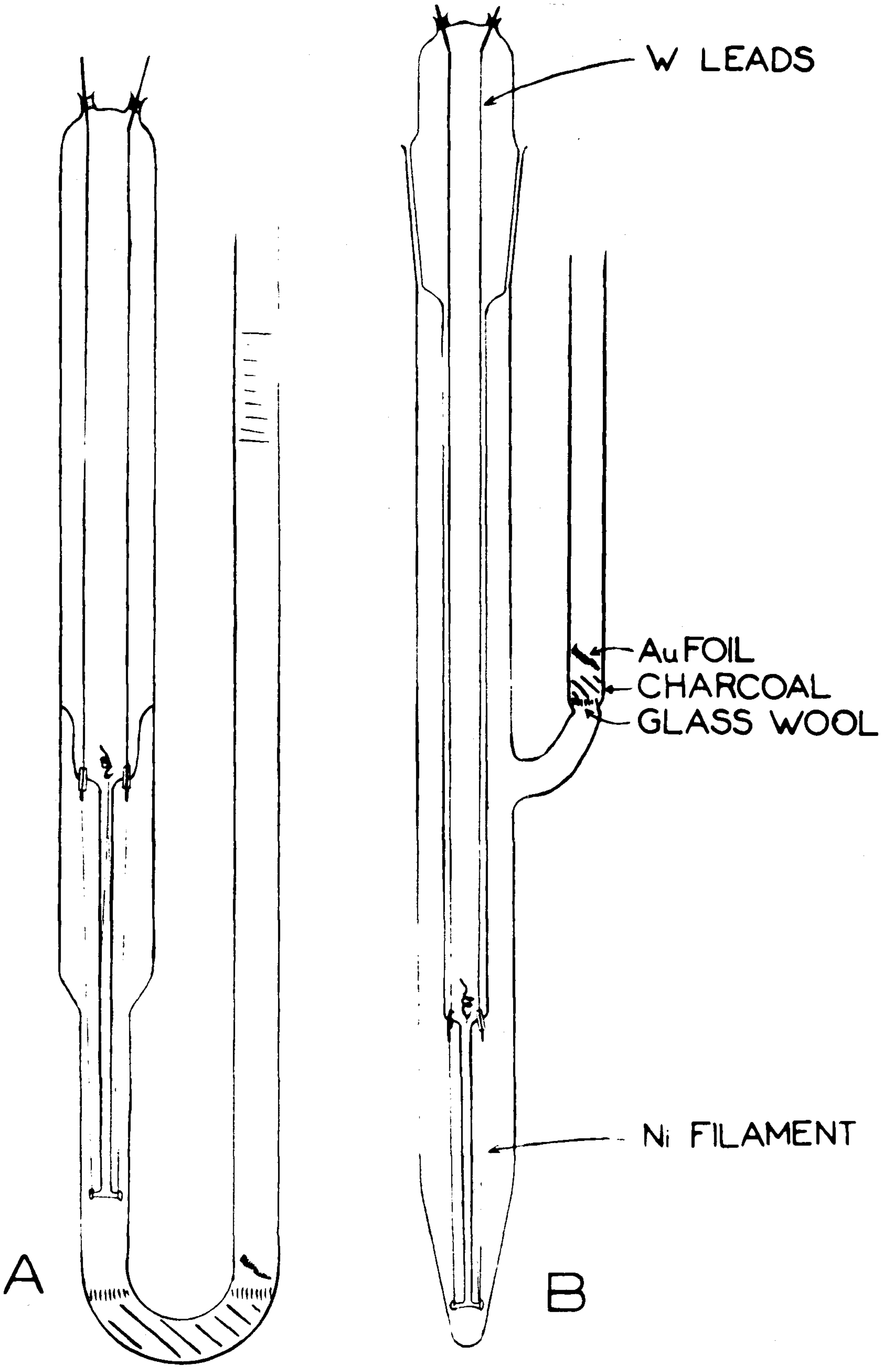


FIGURE 6. PIRANI GAUGES

in contact with the atmosphere. This ensure that the gauges are maintained at constant low temperature, with maximum temperature different between filament and glass wall. The gauges need about two hours to reach stability and even after much longer than this, the light-spot from the galvanometer continues to drift slowly across the scale. Gas is admitted to the measuring gauge via a small ventil remotely controlled for convenience of operation; the compensating gauge is maintained under vacuum throughout an experiment. In measuring the deflections obtained on the scale allowance is made both for the drift and for the non-linearity of response in certain parts of the scale. Previous work[31] had shown that readings at the end of the scale were otherwise about 6 per cent higher than in the centre.

The type of Pirani gauge initially used has certain disadvantages in construction inherent in the design, notably in the difficulty of making a ring seal after the filament has been placed in position. This trouble held up experimental work at one period and eventually a modified design was adopted (Figure 6B). This has the great advantage that the filament can be replaced without constructing a new gauge. No design is trouble-free, however, and at a later stage considerable difficulty was experienced with the Pirani arrangement. As a result of this, one can usefully tabulate certain details which appear essential for the construction of such sensitive gauges which may otherwise be extremely responsive to microphonics:-

(a) Tungsten-pyrex seals must be made without allowing the metal to become brittle.

(b) Tungsten leads through the evacuated centre piece must be insulated from one another and not allowed to touch the glass walls.

(c) The nickel tape must ride smoothly over the central hook, under a slight tension, and be free from twists.

(d) Nickel is best anchored to tungsten by soft-soldering on to electroplated layers of copper. This sticks most firmly if the tungsten is first cleaned by electrolyzing, with occasionally reversing polarity, in caustic soda solution. Low current density is necessary for firm copper-plating.

(e) The total tension applied to the nickel tapes should be of the order of 20 gms.

A theoretical treatment of the behaviour of a Pirani gauge as used in our experiments is given elsewhere in this thesis.

IIg. The Calibration System

For calibration of the Pirani gauges, it is necessary to introduce accurately-known amounts of helium (or neon) into the measuring gauge. These quantities of calibrating gas must be of the same order as the volume being measured and this is achieved by a pipetting arrangement of the type shown in Figure 7.

In order to obtain the necessary amount of helium, the whole calibrating system is first completely evacuated. The mercury is then raised until it is just below the lip of the upper pipetting cup, and spectroscopically pure helium introduced from a reservoir, via a pressure-reducing arrangement, through the tap A. The mercury level is finally adjusted so as to be immediately below the lip of the cup and the pressure difference between the mercury in the two

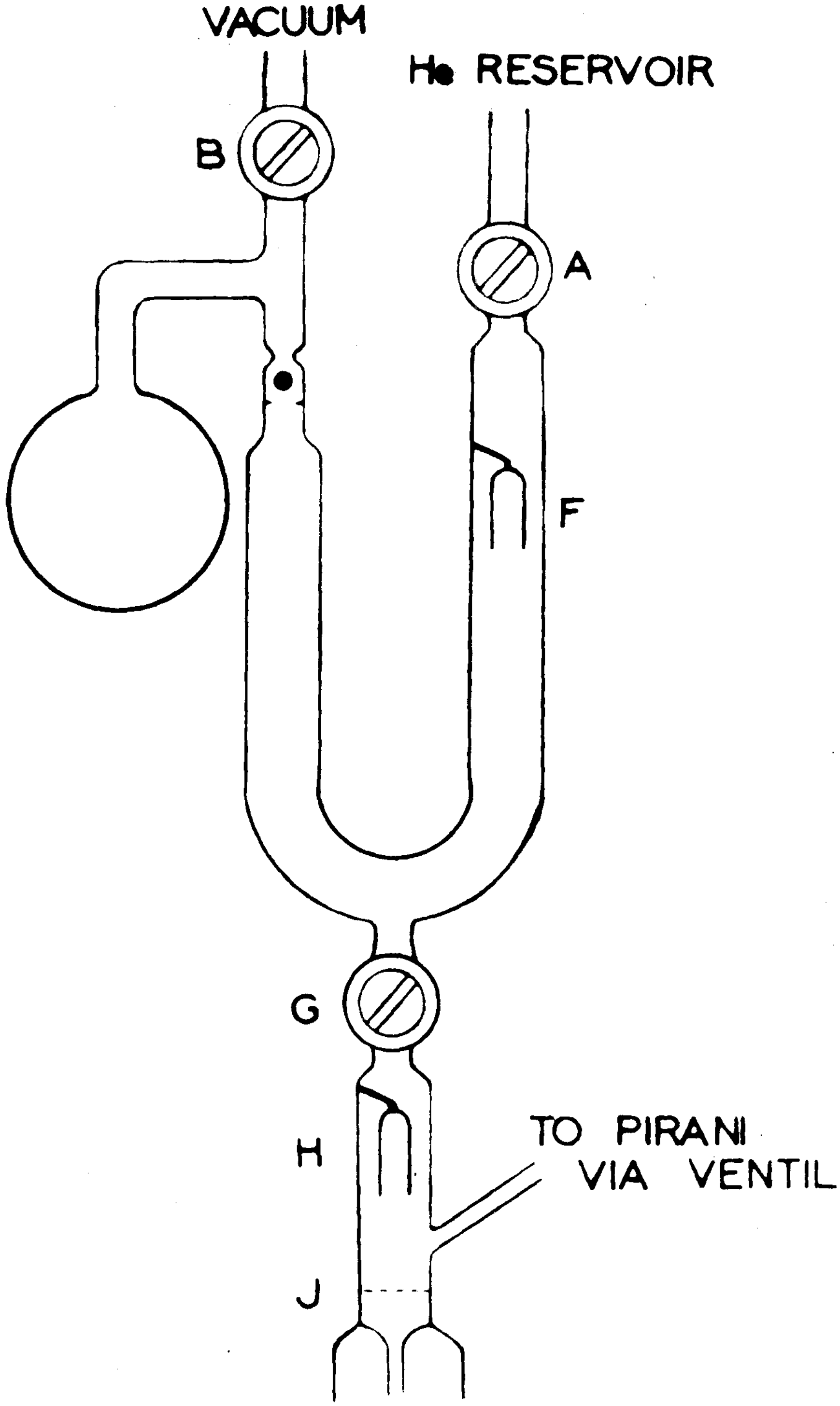


FIGURE 7: PIPETTING SYSTEM

limbs of the apparatus measured. This is done with an accurate cathetometer, reading to 0.001 cm., the average of two readings being taken, and at the same time the room temperature is noted. The mercury is then raised above tap A, trapping the cupful of helium in F and A is closed, a small amount of mercury being left above A to form the additional precaution of a mercury seal. By lowering the mercury to a point just below the lip of cup H, the gas from F is allowed to expand into the volume defined by the mercury meniscus and the closed stopcocks A and ~~C~~ B. After allowing ~~the~~ approximately ten minutes for the gas to attain equilibrium, the mercury level is raised slightly to retain the volume of gas in the pipette, whilst the remainder is pumped away to waste through B, ~~and C~~. When this has been accomplished, tap C is closed and the gas allowed to expand once more into the total volume given by the mercury level-tap A - tap ~~C~~ D. The gas is now at the requisite pressure and aliquots are taken by raising the mercury above tap G, closing this tap and lowering the mercury to the etched ring J so that the gas from the pipette can expand into the Pirani dead-space and thence into the measuring gauge through the ventil. Thus for all measurements, the mercury is aligned with the mark at J to ensure a constant volume.

Two slightly different pipetting systems have been employed in this work, but the principles involved in calculation of the final volume of gas delivered to the gauge are the same in both cases. We shall consider firstly the earlier arrangement using the figures quoted by Wilson[31], from earlier work by Glückauf.

Volume of pipette F = 1.0313 ccs.

Volume of pipette H = 1.0141 ccs.

Volume for expansion = 403.15 ccs.

Now at pressure 'p' mm., as measured with the cathetometer, the amount of gas in F is equal to $\frac{p}{760}$ x 1.0313 ccs. at 760 mm. pressure.

When expanded into a volume of 403.15 ccs., and 1.0141 ccs. of this taken, we have $\frac{p}{760}$ x 1.0131 x $\frac{1.0141}{403.15}$ at 760 mm. pressure.

This latter process is repeated, so that finally one obtains:

$$\frac{p}{760} \text{ x } 1.0131 \text{ x } \left(\frac{1.0141}{403.15}\right)^2 \text{ ccs. at 760 mm. pressure}$$

After correcting this to 0°C. from a room temperature T°K., we have for the final volume introduced into the gauge:

$$\frac{p}{760} \text{ x } 1.0313 \text{ x } \left(\frac{1.0141}{403.15}\right)^2 \text{ x } \frac{273}{T} \text{ ccs. at N.T.P.}$$

Room temperature is assumed to remain constant; during the course of a typical determination, this rose from 22.7°C. to 23°C. and such temperature fluctuations are negligible within the limits of the experiment.

IIh. Calibration of a New Pipetting System

The pipetting system originally installed in the apparatus proved satisfactory until the end of September 1950 when the calibration figures showed a disquieting lack of consistency. For example, a typical set of deflections was 10.27, 9.51, 9.85 cms. to be compared with the agreement previously found, as in 6.45, 6.47, 6.39 cms.

This effect persisted, and even worsened, and various factors which might possibly affect the volume of gas delivered were systematically examined.

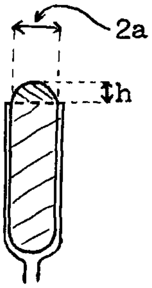
The time allowed for the gas to reach equilibrium was varied to no effect, and regreasing all the taps associated with the system equally failed to cure the trouble. The reservoir of helium was removed in case it had become contaminated with air and was replaced with a new bulb, to no effect. Calibration figures obtained with pure neon showed no better consistency. To ensure that the errors did not originate in the galvanometer circuit, a 5 ohm. resistance was fitted across two adjacent terminals in the resistance box so that on connecting a mercury switch, a deflection was obtained on the scale. By this means it was possible to show that the scale correction was reliable and the sensitivity of the galvanometer was not changing. Furthermore, the fitting of the two new Pirani gauges produced no improvement.

It was therefore decided that the error was inherent in that particular pipetting system and a new apparatus was built and calibrated, and the trouble was eliminated. No satisfactory explanation for the breakdown of the original system is easily forthcoming. One possibility is that the glass walls had become saturated with the helium at high pressures, followed by desorption at lower pressures. It has also been suggested that grease had been forced onto the walls and into the pipetting cups, from the taps, by the mercury and was in some way causing anomalous desorption and adsorption effects. Certainly the inside of the system showed signs of surface contamination of some nature.

One change was made in the design of the new expansion system. A ground ball valve was used at G (see Figure 7) to retain the mercury at this point instead of closing the tap formerly present in order to minimise the contact of mercury with tap grease. This valve is controlled by a lever-operated permanent magnet. The small pipette cups were constructed from ordinary soda glass tubing, closed at one end and sealed into the appratus with a piece of glass rod. The open end is ground flat with carborundum powder to be perpendicular to the side of the tube. The volume of these pipette cups was determined by measuring the weight of mercury which they contained when exactly filled; that is to say, the volume of the cup defined by the ground glass surface. Two methods of determining this volume were used. One system was to fill the cup until such an excess of mercury was present to form a large convex meniscus and then remove this excess quickly with a sharp thin metal blade (a clean safety razor-blade is excellent for this purpose), thus obtaining the volume defined by the ground face of the cup by pressing down on the grinding with the blade. The alternative method is to allow a small meniscus to form, as near to a 'cap' of a sphere as possible, and then measure the height and diameter of this with a travelling microscope. The volume of such a 'cap' is given by

$$V = \frac{1}{6} \pi h \left(h^2 + 3a^2\right)$$

where 'h' and 'a' have the significance shown in the diagram.



The results obtained for cup B by these two methods are shown in Tables 3 and 4. Both groups show good internal agreement and although the agreement between the two methods is not as high, it is satisfactory and removes any uncertainties in the more direct measurements. Consequently for the calibration of cup A, this technique alone was used, with results shown in Table 5.

TABLE 3

Calibration of Pipette Cup B

Weight of cup + Hg (gm.)	Weight of cup (gm.)	Weight of Hg (gm.)	Volume of cup (ccs.)
16.3920	3.7179	12.6741	0.935_8
16.4080	3.7180	12.6920	0.936_4
16.4146	3.7181	12.6965	0.937_4
16.4162	3.7181	12.6981	0.937_5
16.4143	3.7181	12.6962	0.937_5
16.3939	3.7080	12.6959	0.937_4

Temperature during measurements - 21°C.
Corrected average value - 0.9372 ccs.

TABLE 4

Calibration of Pipette Cup B by alternative method

Weight of cup + Hg (gm.)	Weight of cup (gm.)	Weight of Hg (gm.)	Total Volume (ccs.)	h (cms.)	a (cms.)	Volume of 'cap' (ccs.)	Volume of cup (ccs.)
16.7005	3.7225	12.7980	0.957_7	0.148	0.285	0.020_9	0.936_9
16.5975	3.7196	12.8756	0.950_1	0.111	0.285	0.015_1	0.935_0
16.7195	3.7195	13.0000	0.959_4	0.156	0.285	0.022_2	0.937_2

Temperature during measurements - 21°C.
Average value - 0.9364 ccs.

The total expansion volume of the calibrating system was found by measuring the pressure changes when a known volume of air at atmospheric pressure was allowed to expand into the evacuated apparatus. The reference volume was the volume enclosed between the taps A and B (see Figure 8) and included the volume of the bore of the key of tap B. This total volume was found by weighing, by difference, the weight of distilled water which it would hold, with the results shown in Table 6.

The first experimental arrangement tried is shown in outline in Figure 8. The manometer was constructed of wide bore tubing (internal diameter 2.0 cms.) to exclude any surface tension errors in pressure measurements. The whole apparatus was erected vertically by comparison with a plumb-line. Such a manometer had the additional advantage of presenting a practically flat meniscus, easily aligned with the cross-wire of the cathetometer used for pressure measurements; each final pressure reading was the average of at least three experimental readings. One drawback was that the vertical travel of the cathetometer was less than 40 cms., so that all measurements were made above and below a reference line on the manometer tubing. Each experiment began with the whole apparatus at atmospheric pressure; taps A and B are then closed and the remainder completely evacuated, the vacuum being checked with a MacLeod gauge. The manometer then shows barometric height, since the one side is open to the atmosphere (the looped end prevents dust reaching the surface of the mercury). This pressure is measured, after which D is closed, isolating the system from the main vacuum line and C opened with the mercury level immediately below the lower pipette cup. This level needs to be adjusted after each operation to ensure constant volume at the various

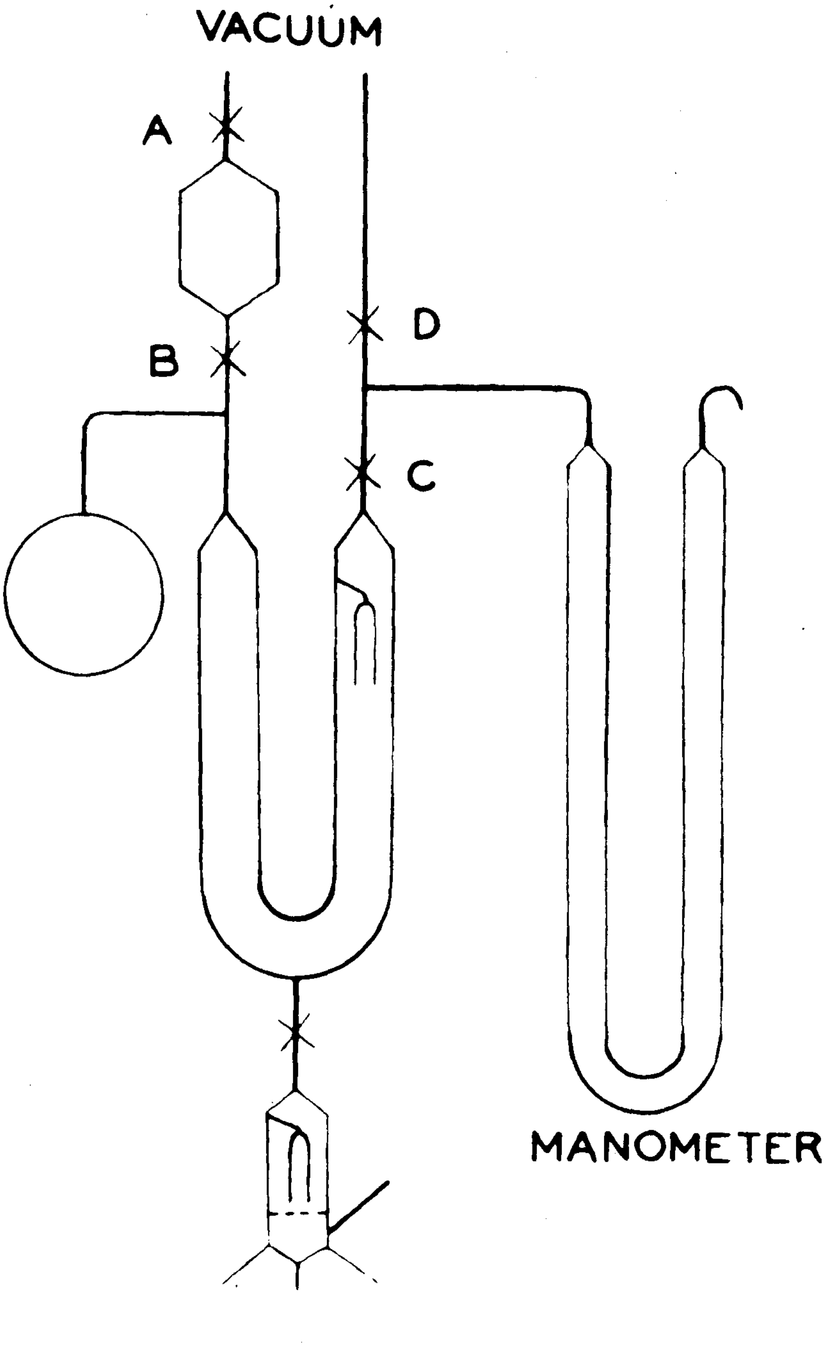


FIGURE 8

TABLE 5

Calibration of Pipette Cup A

Weight of cup + Hg (gm.)	Weight of cup (gm.)	Weight of Hg (gm.)	Volume of cup (ccs.)
17.4471	4.5594	12.8877	0.951_3
17.4592	4.5527	12.9065	0.952_7
17.4539	4.5528	12.9011	0.952_3
17.4504	4.5527	12.9877	0.952_0
17.4438	4.5527	12.8911	0.951_6
17.4473	4.5525	12.8948	0.951_8

Temperature during measurements - 18°C.
Average value - 0.9520 ccs.

TABLE 6

Determination of volume of reference volume

Weight of vessel water (gm.)	Weight of vessel alone (gm.)	Weight of water (gm.)	T°C	Volume of water (ccs.)
143.196	86.679	56.517	18	56.595
139.260	82.731	56.529	19	56.618
139.787	83.266	56.521	19	56.611

Average value 56.608 ccs.

pressures. When the new pressure has been measured, the manometer space is evacuated by closing C and pumping gas away through D. Expansion of the gas in the main body of the apparatus into this evacuated volume, tap D now being closed, gives a second pressure reading. This latter cycle can be repeated any number of times, but in fact such a procedure may lead to one experiment yielding two results for the total volume whilst one in which the initial expansion is as statistically accurate only gives a single value. Generally only one expansion was carried out.

Now suppose atmospheric pressure = p_1

Volume A and B (including the bore of B) = v_1

Volume to be measured = v_2

Volume of the manometer space (including the volume between D & C) = v_3

Then on the first expansion, one has

$$p_1 v_1 = p_2(v_1 + v_2 + v_3)$$

where p_2 is the total pressure in the system after the expansion. Since p_1 and p_2 are both measured and v_1 is already known, a value for $\overline{v_1 + v_2 + v_3}$ is obtained.

On the second expansion, since v_3 only has now been evacuated

$$p_2(v_1 + v_2) = p_3(v_1 + v_2 + v_3)$$

from which $\overline{v_1 + v_2}$ can be obtained.

Similarly, for a third expansion

$$p_3(v_1 + v_2) = p_4(v_1 + v_2 + v_3)$$

giving a further value for $\overline{v_1 + v_2}$

The manometer space does not remain constant, but varies with the height of the mercury column and so all pressure readings were corrected to constant volume. The standard adopted was the volume available when the first expansion reading is taken. For this purpose, an approximate value of 400 ccs. for $\overline{v_1 + v_2}$ was used, and the volume per unit length of the manometer tubing found by measuring the height of a volume of water of known volume. The bore of the tube was found to be sensibly constant. Thus to correct a pressure of p cms. to constant volume a volume of p.u must be allowed for (where u is the volume per cm. of the tube). The correct pressure, p', is then given by:

$$p' = p. \frac{400}{400 - p.u}$$

The results obtained by such a procedure are shown in Table 7. The mean value obtained for $\overline{v_1 + v_2}$ is 404.42 ± 4.1 ccs. on the first analysis, and even when the result of experiment 6 (392.46 ccs.) is removed, the value is 405.7 ± 3.3, giving a percentage accuracy of 0.81 per cent which is far from satisfactory. Correlation for $\overline{v_1 + v_2 + v_3}$ is slightly better, the accuracy being 0.42 per cent (520.9 ± 2.2 ccs.). Errors due to fluctuations in room temperature can be ruled out, since for every pressure reading a corresponding reading was taken on a thermometer suspended between the limbs of the pipetting system; temperatures remained practically constant throughout a series of measurements and indeed varied little between separate experiments. One source of error may have arisen in the actual experimental procedure; since each pressure as given is the difference of the measured barometric height and the atmospheric pressure reading, one is finding a comparatively small pressure (about 8 cms. on the first expansion) as the difference of two much larger ones.

A new approach to the problem was therefore attempted, using a method of measuring pressures illustrated diagrammatically in Figure 9. Instead of leading through tap D to vacuum, an arrangement of taps allowed, firstly, atmospheric pressure to be measured by opening D and E to vacuum and G to the atmosphere with F remaining closed. Tap G is then closed and both sides of the manometer evacuated by opening F to vacuum. For expansion, D is closed and the pressure in the pipetting system directly shown between the two limbs of the manometer. This has the extra advantage that the pressure reading can be measured using only a small travel on the cathetometer. As before, values for the volume of the manometer space can be obtained by closing C and pumping gas away through D before carrying out expansions into this space. Taps F and G must be closed throughout this process. This procedure is considerably quicker than was the case in the first series of experiments. The results obtained by this method are shown in Table 8; the figure of 412.12 ± 0.85 ccs. for $\overline{v_1 + v_2}$ has a percentage of accuracy of 0.21 per cent and for $\overline{v_1 + v_2 + v_3}$, 647.88 ± 0.98 (0.15 per cent), much better than from the previous series of experiments. From this final value for $\overline{v_1 + v_2}$ one must subtract the previously found volume of v_1 (= 56.608 ccs.) and the volume of the bore of tap B. This was measured by sealing one end of the bore with cellulose tape and finding, by difference, the weight of mercury it would contain, leading to a volume of 0.28 ccs. (Actually found as the average of two experiments 0.281 ± 0.002). This gives a final value of 355.23 ± 0.85 ccs. (0.24 per cent) for the total expansion volume.

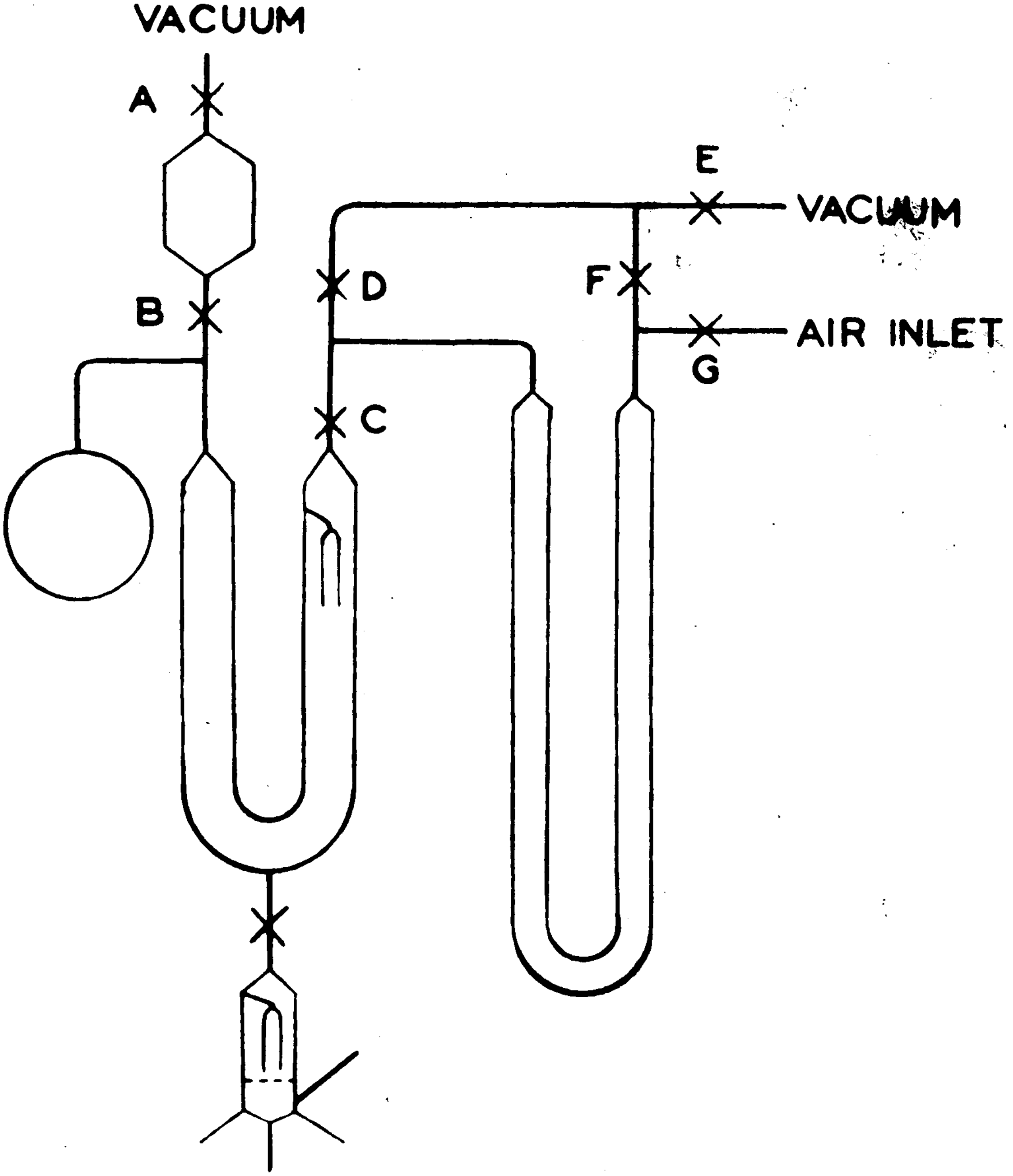


FIGURE 9

Hence for the new pipetting system, one has:-

Volume of upper cup (A) = 0.9520 ccs.

Volume of lower cup (B) = 0.9370 ccs.

Total expansion volume = 355.23 ccs.

Substituting into the calibration formula as before, we have:-

$$S_{He} = \frac{\frac{p}{760} \times 0.9520 \times \frac{(0.9370)^2}{(355.23)} \times [T/273]}{\Delta}$$

$$= \frac{p}{\Delta} \times 8.716 \times [T/273] \times 10^{-9} \text{ ccs. cm.}^{-1}$$

After installation and out-gassing, the new pipetting system proved quite satisfactory. In view of the difficulties experienced in this calibration, it would be interesting to discover the accuracy of the figures quoted by Wilson for the old calibration system, and to know whether previous workers had experienced the difficulties encountered in the work described.

IIi. Oxygen Purification and Storage System

In order that oxygen may be used as a carrier gas, it is necessary to purify the gas from both helium and neon and means must be provided both to store the purified gas and to supply it to various parts of the apparatus. Previous workers had prepared pure oxygen by the catalytic decomposition of hydrogen peroxide with platinum black, but this process has the disadvantage of being slow, needing about one hour to prepare two litres of gas. A method of purifying oxygen as normally supplied from cylinders was therefore used throughout this work.

The oxygen purification and storage system is shown diagrammatically in Figure 10. Oxygen enters through tap C. and the T-piece below this must first be flushed clear of air by allowing oxygen to stream through it for about ten or fifteen minutes, passing into the atmosphere through a mercury trap so that back-diffusion of air cannot take place. A further precaution lies in closing the tap B, thus isolating the storage bulb etc. and slowly pumping oxygen and any entrained air away to waste through A. When the T-piece is judged to be completely freed of air, A is closed and oxygen is allowed to flow into the previously evacuated storage bulb by slightly opening taps B and C. The pressure in the system is shown by a manometer G. Excess oxygen bubbles away to waste through the mercury trap already mentioned.

When atmospheric pressure is registered by the manometer, C is closed and the tube D, which contains activated charcoal retained by a 'plug' of glass wool, is cooled in liquid nitrogen. This causes adsorption of oxygen upon the charcoal and the non-adsorbed gases (hydrogen, helium and most of the neon) are removed by the pumping system through A. In practice, the tap A is opened when about half-a-centimetre of oxygen still remains unadsorbed, in order to flush out these gases completely. The adsorbed gas is pumped for about one hour; that which remains after this is allowed to attain room temperature and is then liquified by cooling the tube F in liquid nitrogen. At this temperature (-195.5°C.), the vapour pressure of the oxygen is 16.215 cms., so that by closing the tap E and pumping away all the gas above it, one removes approximately one-fifth of the oxygen, which carries with it practically all the unliquified gas. The system is further flushed out by rapidly opening E momentarily. After repeating this latter process two or three times, tap B is closed and the oxygen allowed to vaporize; this must take place slowly in order to prevent 'bumping'.

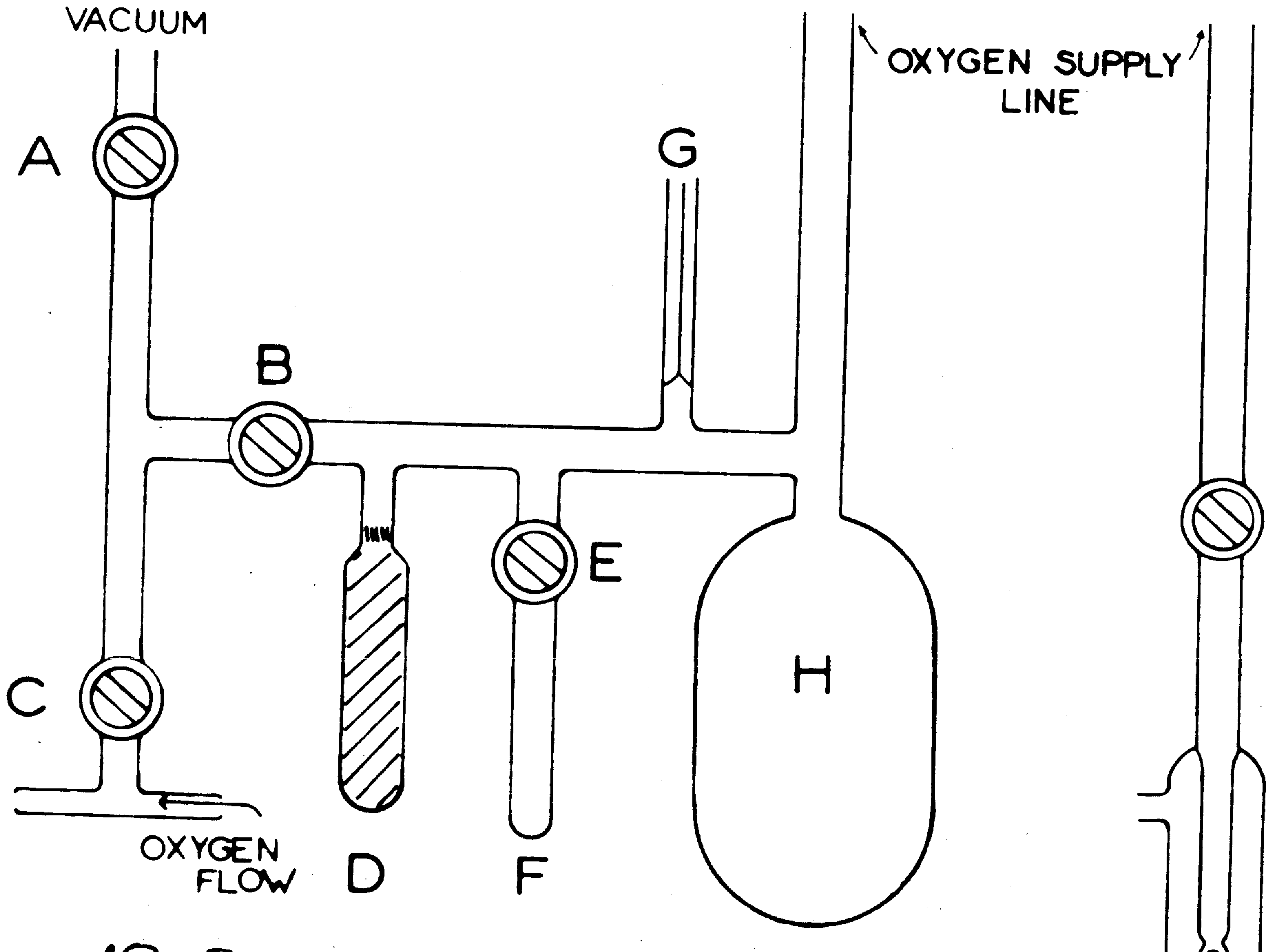


FIGURE 10 OXYGEN SUPPLY SYSTEM

A blank determination is always carried out after each preparation and the process outlined above has been shown to be capable of removing helium and neon down to one part in 10^{11} parts of oxygen. In certain cases, large amounts of inert gas were found, even after a double application of the purification treatment and this was invariably traced to the parent cylinder. Gas in the storage system was repurified by adsorption and pumping at weekly intervals.

When using oxygen as a carrier gas for helium work, it is necessary to pass oxygen into vessels which are evacuated or at low pressure. The type of mercury-steel ball valve used for this is also shown in the diagram; clearly oxygen can pass in one direction only and loss of helium by back diffusion is impossible.

IIj. Special Radiochemical Techniques

Working with radioactive sources involves certain problems and techniques not encountered in normal chemical practice and a note on these aspects is not inappropriate. The small scale of operation necessitates special manipulative methods and the adverse physiological effects of the radiations emitted calls for careful precautions.

Work with strongly active sources was always carried out in the 'hot' laboratory, for it is important to prevent contamination of low activity measurements being carried out in other laboratories of the department. From the point of view of these latter experiments, the helium laboratory was regarded as 'hot'. Some transference of glassware between these laboratories was unavoidable, but was kept to an absolute minimum.

To avoid harmful physiological effects, strongly active sources were always handled behind lead bricks, generally two inches thick, and radium solutions or solids were always surrounded with such shielding. Chemical work in fume cupboards was always in a strong draught, to prevent inhalation of active material in the form of dust or spray. Protective rubber gloves were worn when working with sources above the tracer level (i.e. containing more than about 10-100 microcuries of activity). In order to avoid sucking active liquids into pipettes, these were worked by rubber teats and wash bottles with squeeze bulbs operated by hand to avoid oral contact with glassware.

Radioactive solutions were never poured in order to prevent contamination of the outside of the vessels and here again pipettes with rubber teats were used. Centrifugation was used to separate solids and liquids; after centrifuging, the liquid phase can easily be removed with a pipette. It is important to prevent the formation of a spray, which may carry activity, and for this reason, solutions were never boiled when a reduction of volume was necessary, but evaporated on a steam bath.

When working with radium solutions, it is important to use pyrex vessels, centrifuge tubes and pipettes since soda glass adsorbs radium strongly, especially from alkaline solution[32].

CHAPTER III. THE RATE OF FORMATION OF HELIUM FROM RADIUM. EXPERIMENTAL METHODS AND RESULTS

IIIa. Mathematical Introduction

The production of helium in a radium preparation is in part due to the formation and subsequent decay of the α-emitting daughter elements - radon, radium-A and radium-C. We shall assume in what follows that the amount of helium formed by radium-F can be neglected; since radium-D was removed from the sources before they reached us, this is certainly justifiable. Accurate calculation of the helium produced by radium alone is only possible if the solution is initially free from radon and the short-lived daughter products. The conditions for this removal are discussed later.

We shall consider first the method of calculation of Gunther[7], following Rutherford, Chadwick and Ellis[33].

Let rate of formation of He by Ra = x

and by Rn + RaA + RaC = y

i.e. total helium in time 't' = (x + y) t

Now if the active deposit is assumed to reach equilibrium with radon immediately, one can write

$$y = 3x\int_0^t (1 - e^{-\lambda_1 t})dt$$

where λ_1 is the decay constant of radon.

Then Q = total helium in time 't'

$$= xt + 3x\int_0^t (1 - e^{-\lambda_1 t})dt$$

whence $x = \dfrac{Q}{1 - \dfrac{(1 - e^{-\lambda_1 t})}{\lambda_1}}$

Evidently the value of the specific activity follows from 'x'.

IIIb. Calculation of New Formula (Method 1)

The assumptions made in the above calculation, that the active deposit and radon are in equilibrium throughout the whole period of accumulation is not, of course, strictly true. Two different methods of overcoming this have been worked out and will be presented. The following symbols and values will be used throughout:-

$$\mathrm{Ra} \xrightarrow[\lambda_0]{\alpha} \mathrm{Rn} \xrightarrow[\lambda_1]{\alpha} \mathrm{RaA} \xrightarrow[\lambda_2]{\alpha} \mathrm{RaB} \xrightarrow[\lambda_3]{\beta} \mathrm{RaC} \xrightarrow[\lambda_4]{\alpha,\beta} \mathrm{RaD} \xrightarrow[\lambda_5]{\beta}$$

The number of atoms of each species present at time t is N_0 , N_1 , ... N_5

Numerically

λ_1	7.5545×10^{-3}	hr.$^{-1}$
λ_2	13.6355	hr.$^{-1}$
λ_3	1.55181	hr.$^{-1}$
λ_4	2.11109	hr.$^{-1}$

(Note more decimal places are retained than is justified by the experimental accuracy in the measurement of the half-lives, in order to avoid errors due to arithmetical working).

One can assume,

(i) λ_0 is so small that N_0, the amount of radium present throughout the experiment, is sensibly constant.

(ii) λ_2 is so large that RaA is always in equilibrium with Rn and can be considered as decaying instantaneously on formation.

(iii) λ_5 is so small that He produced by Po can be neglected (and see above).

In this method of calculation, (after Mr. G. R. Martin), one proceeds as follows:

At time t, $N_0\lambda_0 t$ atoms of Ra have decayed and if all the daughters were short-lived, compared with 't', this would have given $4N_0\lambda_0 t$ atoms of helium. In fact, one obtains less than this on account of the finite lifetime of the daughter elements, and the number of α's produced is

$$He = 4N_0\lambda_0 t - 3N_1 - 2N_2 - N_3 - N_4 \qquad (3)$$

In other words, a chain stopped at Rn is 3 α's short, one stopped at RaA is 2 α's short and one terminating at RaB or RaC is 1 α short. It remains simply to calculate the values of N_1 etc.

$$N_1 = \frac{N_0\lambda_0}{\lambda_1}\left(1 - e^{-\lambda_1 t}\right)$$

$$N_2 = \frac{N_0\lambda_0}{\lambda_2}\left(1 - e^{-\lambda_1 t}\right)$$

(see assumption (ii))

$$N_3 = \frac{N_0\lambda_0}{\lambda_3}\left(1 - \frac{\lambda_1 e^{-\lambda_3 t} - \lambda_3 e^{-\lambda_1 t}}{(\lambda_1 - \lambda_3)}\right)$$

$$N_4 = \frac{N_0\lambda_0}{\lambda_4}\left\{1 - \frac{\lambda_4\lambda_3 e^{-\lambda_1 t}}{(\lambda_3-\lambda_1)(\lambda_4-\lambda_1)} - \frac{\lambda_4\lambda_1 e^{-\lambda_3 t}}{(\lambda_4-\lambda_3)(\lambda_1-\lambda_3)} - \frac{\lambda_3\lambda_1 e^{-\lambda_4 t}}{(\lambda_3-\lambda_1)(\lambda_1-\lambda_4)}\right\}$$

This is simply following the procedure of Bateman, given in Rutherford, Chadwick and Ellis[34].

Combining these into equation (3), with subsequent substitution and simplification, we have

$$He = N_0\lambda_0\left\{4t - 398.38\left(1 - e^{-\lambda_1 t}\right) + 0.00717 e^{-\lambda_1 t} - 0.0119 e^{-\lambda_3 t} + 0.00472 e^{-\lambda_4 t}\right\}$$

The last terms rapidly become insignificant and can certainly be neglected beyond t = 5 hours, whereupon the equation becomes:-

$$He = N_0\lambda_0\left[4t - 398.38\left(1 - e^{-7.5545\times10^{-3}.t}\right) + 0.00717e^{-7.5545\times10^{-3}t}\right] \quad (4)$$

IIIc. Calculation of New Formula (Method 2)

The second method of calculation, by the present writer, is based on the equation given by Gunther, and previously quoted, i.e.

$$Q = xt + 3x\int_0^t\left(1 - e^{-\lambda_1 t}\right).dt$$

The fallacious assumption as to the rapid equilibration of radon with the active deposit, in fact, merely gives rise to error in the case of RaC. As previously noted above, one can regard RaA as decaying on formation and RaB is, of course, a β-emitter. Hence one can write

$$Q = xt + 2x\int_0^t\left(1 - e^{-\lambda_1 t}\right).dt + F \quad (5)$$

where 'F' represents an integral term giving exactly the helium produced by RaC alone. This latter we can find easily from the equations given by Bateman. Since the solution is initially free from all the radium daughter elements we have the condition that

$$\frac{S_t}{S_\infty} = 1 - \lambda_4\left(ae^{-\lambda_1 t} + be^{-\lambda_2 t} + ce^{-\lambda_3 t} + de^{-\lambda_4 t}\right)$$

Where S_t = quantity of RaC at time t

S = quantity of RaC at equilibrium

Hence $S_t = S_\infty\left[1 - \lambda_4\left(ae^{-\lambda_1 t} + be^{-\lambda_2 t} + ce^{-\lambda_3 t} + de^{-\lambda_4 t}\right)\right]$

By definition, the rate of production of helium by this equilibrium quantity of RaC is 'x'; consequently, the total amount of helium produced by RaC in the time t $= F$

$$= \int_0^t \frac{S_t.\,x}{S_\infty}$$

$$= x\left[t - \frac{\lambda_4}{\lambda_1}.a\left(1 - e^{-\lambda_1 t}\right) - \frac{\lambda_4}{\lambda_2}.b\left(1 - e^{-\lambda_2 t}\right) - \frac{\lambda_4}{\lambda_3}.c\left(1 - e^{-\lambda_3 t}\right) - d\left(1 - e^{-\lambda_4 t}\right)\right]$$

From the values for λ_1, λ_2, etc. given previously, it is obvious that for values of 't' used experimentally (i.e. t 15), all the factors $(1-e^{-\lambda t})$, except the first can be put equal to unity. The constants a, b, etc. are of the type

$$a = \frac{\lambda_2\lambda_3}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)(\lambda_4-\lambda_1)}$$

$$b = \frac{\lambda_1\lambda_3}{(\lambda_1-\lambda_2)(\lambda_3-\lambda_2)(\lambda_4-\lambda_2)} \qquad \text{etc.}$$

and have the numerical values

$a = 0.4750$

$b = -6.2 \times 10^{-6}$ (negligible)

$c = -9.80 \times 10^{-3}$

$d = -5.85 \times 10^{-3}$

Further, inserting the appropriate values for the decay constants in the now simplified equation

$$F = x\left[t - \frac{\lambda_4}{\lambda_1}\cdot a\left(1-e^{-\lambda_1 t}\right) - \frac{\lambda_4}{\lambda_3}\cdot c - d\right]$$

we can write

$$F = x\left[t - 133.70\left(1-e^{-\lambda_1 t}\right) + 0.013 - 0.006\right]$$

$$= x\left[t - 133.70\left(1-e^{-\lambda_1 t}\right) + 0.007\right]$$

Consequently the final equation becomes

$$Q = xt + 2x\left[t - \frac{\left(1-e^{-\lambda_1 t}\right)}{\lambda}\right] + x\left[t - 133.70\left(1-e^{-\lambda_1 t}\right) + 0.007\right] \qquad (6)$$

Equations (4) and (6) can be shown to be identical. The latter, on simplification gives,

$$Q = x\left[4t - \left(2/\lambda_1 - 133.70\right)\left(1-e^{-\lambda_1 t}\right) + 0.007\right]$$

$$= x\left[4t - 398.44\left(1-e^{-\lambda_1 t}\right) + 0.007\right] \qquad (7)$$

In equation (4), as previously written, the quantities 'He' and '$N_0\lambda_0$' bear the same relation to one another as do 'Q' and 'x' in the above equation. The differences in the coefficient of the $(1-e^{-\lambda_1 t})$ term and in the last term are quite negligible, presumably being due to slightly different arithmetical treatment of the values for the decay constants.

IIId. Decay of the Active Deposit

In association with this treatment of the production of helium by radium, it is of interest to calculate the decay of the short-lived active deposit under the experimental conditions. Before the period of accumulation of the helium, radon is continuously removed for five hours, so that we have the situation of the active deposit decaying in absence of its mother element. The amount of RaC, the last α-emitting element in the chain, at time t is then given by[34]

$$S_t = n_0\left(a_1 e^{-\lambda_2 t} + b_1 e^{-\lambda_3 t} + c_1 e^{-\lambda_4 t}\right) \qquad (8)$$

where the λ's have the connotation previously given and the constants have the values

$$a_1 = \frac{\lambda_3}{(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)} = 0.0114$$

$$b_1 = -\frac{\lambda_2}{(\lambda_2-\lambda_3)(\lambda_3-\lambda_4)} = 2.017$$

$$c_1 = \frac{\lambda_2\lambda_3}{\lambda_4(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)} = -1.555$$

Consequently equation (8) becomes

$$S_t = n_0\left(0.0114e^{-13.636t} + 2.017e^{-1.552t} - 1.555e^{-2.111t}\right)$$

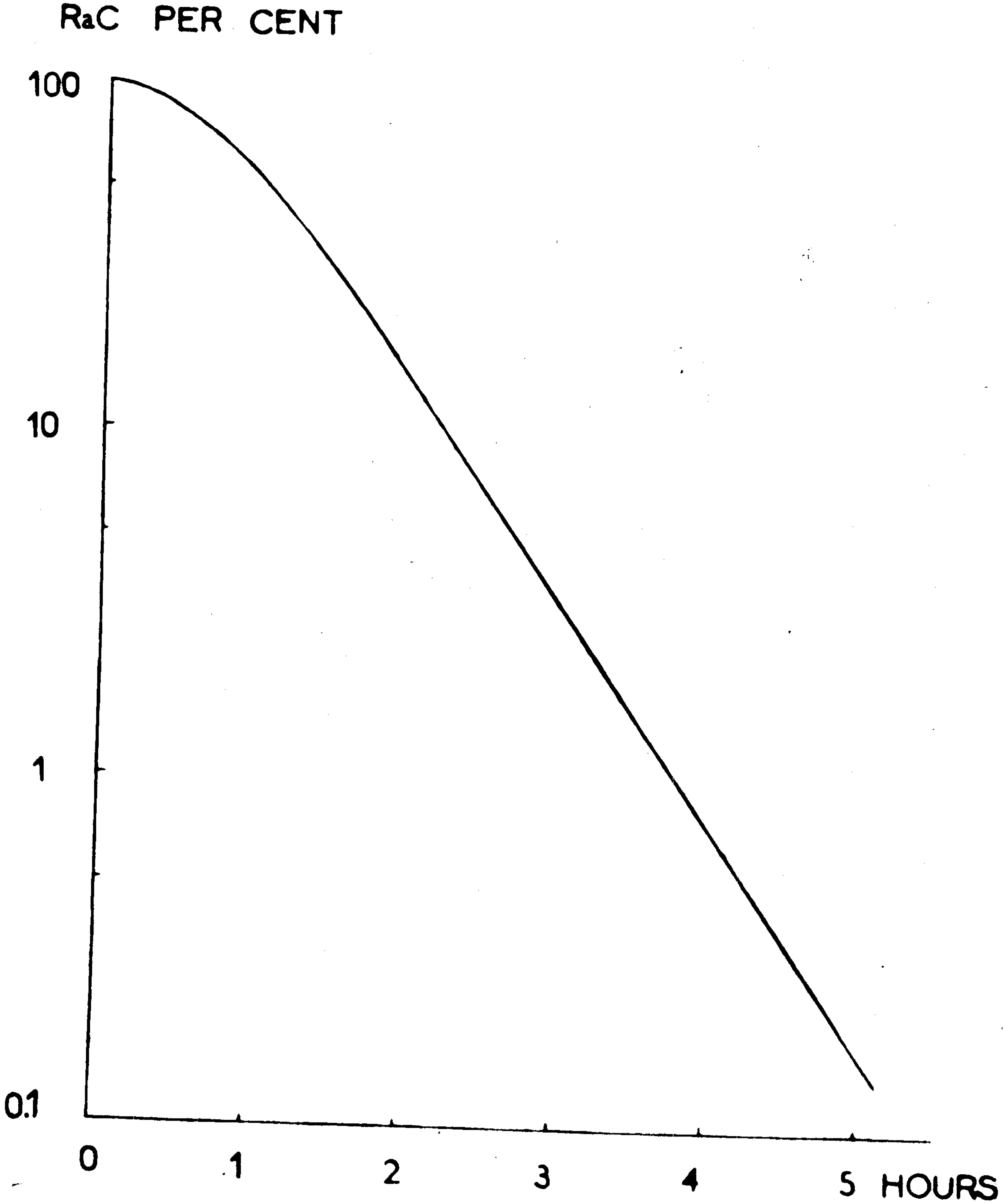


FIGURE 11

Putting $S_t = 100$ per cent at time $t = 0$, we obtain the graph given in Figure 11. The amount of RaC present after 5 hours degassing is of the order of 0.2 per cent. It is interesting to note that after about 2 hours the decay of RaC takes place with an apparent half-life of approximately 25.2 minutes instead of the half-life (in the pure state) of 19.7 minutes.

IIIe. Helium Production by Radium Solutions

An examination of the techniques available for investigating the rate of production of helium from radium suggested that the most promising method was the use of an aqueous solution of a radium salt. Preliminary experiments were performed with a solution containing 8 mg. of radium as radium bromide; in later work, solutions of radium chloride were used. The type of apparatus used throughout this series of experiments on aqueous solutions is shown in Figure 12A. It consists of a system for generating electrolytic gas, which passes through the solution, carrying the gases formed therein through a cooled charcoal tube into the appropriate part of the apparatus.

It is necessary that at the beginning of the period of accumulation of helium the solution shall contain radium free from its daughter products, in order to simplify calculation of the results. Clearly all traces of helium must be likewise eliminated. Mathematical considerations (see previous sections) show that to achieve the required absence of the α-active daughter elements of radium, radon must be continuously removed for five hours along with helium formed during this period. Consequently the first part of an experiment consists of passing electrolytic gas through the solution for five hours and pumping the gases away to waste, after removing radon on the cooled charcoal. After this procedure, all taps are closed and the solution is frozen in order to prevent escape of emanation, which would otherwise pass into the gas phase where active deposit would form on the walls of the vessel. This would result in a certain unknown fraction of the α-particles from the active deposit being stopped in the glass and hence not being collected for measurement as helium. When the period of accumulation of helium is complete, the solution is quickly melted and again degassed with electrolytic gas, which carries helium into the circulating system, after addition of oxygen.

Electrolytic gas is generated from sodium hydroxide solution, which is evacuated, in order to remove dissolved air, before being placed in position. A suitable potential is obtained from a 2 volt battery; a rheostat of the order of 50 ohms maximum resistance is placed in series in order to control the current. It was found that if the caustic soda solution is too strong, violent bumping is liable to take place during electrolysis under vacuum and if the concentration is too low, frothing occurs. Both these effects result in alkaline solution passing down the central tube into the radium solution below. A reasonable compromise is obtained by using an approximately normal solution of sodium hydroxide. One further factor is the pumping rate, which can cause frothing if too high, especially during the initial five hour degassing period; this can be controlled to a certain extent by only partially opening the relevant stopcocks on the main vacuum system. The vacuum electrolysis of caustic soda solution takes place more smoothly if the nickel electrodes are 'activated' occasionally by electrolysis in dilute hydrochloric acid, alternately reversing their polarity. It seems probable that long standing in alkali has the effect of removing from the surface those centres at which bubbles of gas form most easily.

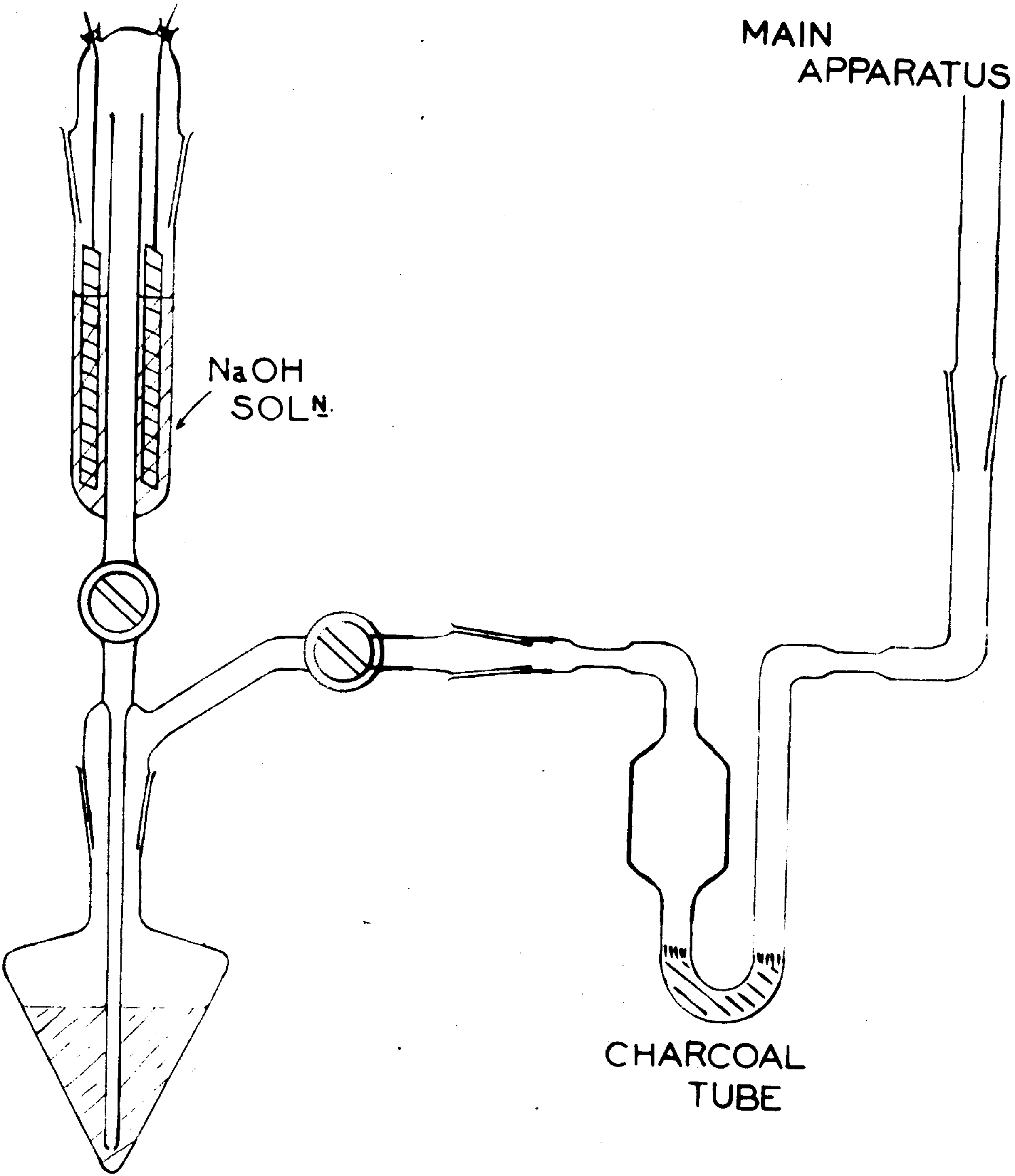


FIGURE 12A

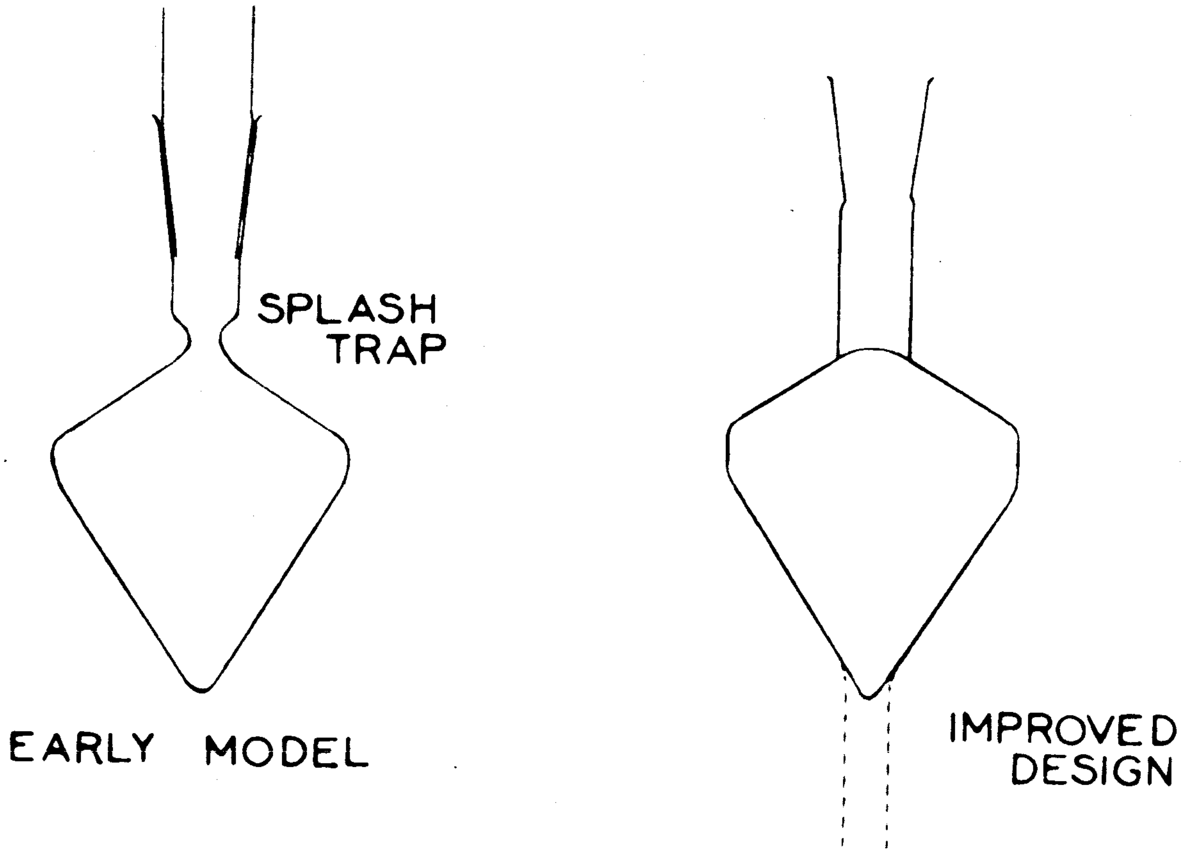


FIGURE 12B

The conical form of the vessel containing the radium solution minimises strain consequent upon the expansion of the solution on freezing. Early models had a constricted neck to prevent loss of solution by splashing. Although this was efficient in itself, it was found that any drops of liquid which did pass beyond the constriction were retained above it by surface tension. The constriction was therefore abandoned and splashing minimised by a lengthening of the neck of the vessel. The flasks which were employed for transporting radium chloride solution from the Radiochemical Centre to Durham are shown in Figure 12B. The solution is pipetted into the inverted flask through the tube and retained by the thin glass septum. After washing down with water, the tube is carefully sealed at A to form a conical vessel and the seal carefully annealed. When needed for use, the septum is carefully pierced with a glass rod. It would probably be unsafe to use this system if the solution were to be stored over long periods because of the pressure build-up of gases formed by radiolysis of the solution. All glass vessels were treated before use to fix any free sulphate in the glass, in order to prevent formation of the insoluble radium sulphate. The flasks were filled with barium chloride solution, allowed to stand overnight and then thoroughly washed with distilled water.

The removal of radon from the gas stream, whether flowing to waste or into the circulating system, is important for two reasons. Firstly because the presence of radon and its daughter products in the atmosphere would consistute a considerable health hazard; secondly because its presence inside the apparatus is equally undesirable. It was shown, by gamma activity measurements, that radon could be removed completely by adsorption on charcoal cooled in Drikold (solid carbon dioxide). It is hoped to discuss the adsorption of radon on charcoal elsewhere[35]. Oxygen is condensed but slightly under these conditions. Charcoal tubes were activated prior to use by heating to approximately 150°C. for some hours in vacuo. Each tube contained of the order of 0.5 gm. of B.D.H. activated charcoal. When the degassing is complete, the tube can be sealed under vacuum by heating at the constrictions shown. The used tubes were retained behind walls until their γ-activity had fallen to a safe level for normal storage.

During the comparatively long time of the initial outgassing of the solution, considerable amounts of water were found to be frozen out in the charcoal tube. This arises partly from distillation from the solution itself and partly from the electrolytic gas which is saturated with water vapour at its genesis. The distillation effect can be minimised by cooling the radium solution in an ice-bath, but despite this, trouble was still experienced with blockages in the charcoal tubes. Bulbs containing potassium hydroxide pellets or silica gel were placed before the charcoal tube, but with little effect. Eventually, the inlet side of the tubes were widened to allow condensation without blocking the flow of gas: the region of condensation could be controlled to a certain extent by adjusting the level of the surrounding Drikold. Such difficulties do not occur during the transfer of helium into the apparatus for measurement, since the time involved is much shorter (usually about 15 minutes) and tubes of uniform diameter were used.

IIIf. Preliminary Experiments : 8 mg. Radium Bromide

When the present series of experiments were first discussed,no pure radium salt was easily available. For this reason, and in order to gain experience of the method, certain preliminary experiments were carried out, using a solution of commercially pure radium bromide. This contained 8 mg. of radium measured by γ-activity determinations. The solution was initially yellow, but on evacuating for the first time, this colour disappeared and a brown condensate appeared in the neck of the cooled charcoal tube; this was almost certainly bromine, resulting from the radiolysis of radium bromide by its own α-particles.

Only three experiments were carried out before purer solutions became available, when this preliminary work was discontinued. In the second of these, the time of accumulation was abnormally long, due to delays which prevented the accumulated gas being flushed into the apparatus. Consequently, the amount of helium was measured fractionally, with some resultant loss in precision. The excellence of the agreement between the three results (see Table 9) may therefore be somewhat fortuitous. The values given for the specific activity have no absolute significance since, as noted above, the amount of radium present was not known to the required accuracy.

TABLE 9

Radium specific activity : solution of 8 mg. $RaBr_2$

	Time of Experiment (hrs.)	Vol. of He found (ccs. of 10^6)	Specific activity (α/sec./gm. x 10^{10})
1	21.0	1.02	3.73
2	156.0	13.31	3.77
3	44.50	2.55	3.68

When the experiments with radium chloride solutions were resumed, it was found that surprisingly large quantities of helium were being obtained from the solutions. From the earlier results it appeared that the excess depended on the solution used: for the 1.01 mg. solution, excesses of the order of 20 per cent were found: for the stronger source, the excess was in the region of 70 per cent. Subsequent experiments (see Table 11) however, demonstrated clearly that it was the time allowed for accumulation of helium which was the critical factor in determining the apparent specific activity of the sources.

Possible errors arising from faults in the apparatus were eliminated at an early stage; additionally, the distribution characteristics of the fractionating column were checked and found to be unchanged. No contamination of air occurred in any of the experiments. Diffusion of atmospheric helium into the vessels during accumulation of radiogenic helium could not be invoked in explanation. Suspected blocking of the cooled charcoal tube with water vapour (see Section IIIe) was shown not to be the cause of helium being retained during the five-hour outgassing period. Finally, it was suggested

TABLE 11

Radium chloride solutions : helium production

	Strength (mg. of Ra)	Time (hrs.)	Volume of He (ccs. x 10^6)	Theoretical He Yield (ccs. x 10^6)	Excess He (ccs. x 10^6)	% Excess
1	1.01	125.0	1.52	1.28	0.24	18.8
2	1.01	128.4	1.62	1.32	0.30	22.7
3	8.24	20.5	1.63	1.01	0.62	61.3
4	8.24	18.75	1.62	0.91	0.71	78.3
5	1.01	22.0	0.21	0.109	0.10	90.8
6	1.01	144.7	1.90	1.56	0.34	21.5
7	1.01	19.0	0.21	0.092	0.11	123.0

that the presence of hydrogen in the bubbler during the accumulation period might cause desorption of helium from the walls of the vessel, more especially since one could expect comparatively large quantities of helium to have been formed in the walls as a result of the decay of radon and the active deposit in the gas phase above the solution. To check this point, the weaker solution was transferred to a completely new vessel and electrolytic generator, between experiments '2' and '5' (Table 11). Results showed no decrease in helium yields.

It was then decided to compare the γ-activities of the two solutions, at a time such that the stronger was at equilibrium. The growth of the γ-activity of the weaker solution was followed: since the time after sealing this latter was known, it was possible to calculate the equilibrium γ-activity. Results shown in Table 12 were obtained by placing the bubbler containing the solution in a fixed glass container, at a distance of 155 cms. from a bell-type counter. The Geiger tube was mounted inside a lead castle whose door was left open. Since both solutions were of nearly equal volume in identical vessels, geometrical errors could be neglected. In the initial experiment, the ratio of the γ-activities of the two solutions was far from that expected but grew closer to the theoretical value as the daughter products of radium grew to equilibrium in the weaker solution. The last measurement shows both the actual and corrected ratios approaching the theoretical value, within the accuracy of the experiment. The small Geiger tube used is, of course, far from ideal for the comparison of solutions of γ-emitting nuclides.

TABLE 12

Comparison of γ-activities of solutions of radium chloride

Solution A : 8.24 mg. Ra in equilibrium with its immediate daughters

Solution B : 1.01 mg. Ra, daughter elements growing to equilibrium

Time 't' after sealing B (Days)	$\frac{\text{Activity A}}{\text{Activity B}}$	$\frac{\text{Activity A}}{\text{Activity B}}(1-e^{-\lambda_1 t})$
2.97	13.6	5.70
4.74	12.5	6.37
7.0	10.1	7.25
12.97	9.08	8.36

One explanation which could correlate these results and those on the rate of helium production was that the mother solution from which the sources were taken had been contaminated in some way with another α- and γ-emitting isotope. This was suggested with reluctance, since extremely careful techniques had been used in its preparation at the Radiochemical Centre, Amersham. Radiographic methods were used to examine the range of the α-particles emitted. The washing liquor was available from the transfer of the 1.01 mg. solution to a fresh vessel referred to above, and although its γ-activity was negligible, it contained sufficient radium to give a reasonable number of tracks. A drop of the solution was placed on an Ilford nuclear emulsion plate, left for 5 minutes, and the plate thoroughly washed. It was then left overnight in a desiccator, developed, fixed and dried. Examination revealed several well-defined tracks:

measurements of their lengths were made with a medium-power microscope and a correction applied for shrinkage in the horizontal plane of the plate. Many single tracks corresponding to the α-particles from radium were observed and several stars from radium and its daughters, as far as radium-C'. Although tracks were observed which could not be definitely identified as α's from radium or its daughters, no evidence of gross contamination was obtained. In particular, there were no long tracks corresponding to the highly energetic α-particles from thorium-C', indicating absence of members of this decay series.

A further experiment followed the decay of the active deposit by allowing this to grow from the condensed gases swept out of the solution. The stronger solution was degassed in the usual way for five hours and the gases passed through the first of two U-tubes in series (see Figure 13). This charcoal tube was cooled in Drikold whilst the second tube remained at room temperature. At the end of the out-gassing period, the solution was frozen: the tubes were sealed at points 'a' and 'c' and tube A allowed to reach room temperature whilst B was cooled in liquid nitrogen. In this way, gaseous products were removed from A, leaving the active deposit. The presence of some water in A proved rather troublesome, but eventually this too passed over to tube B. The tubes were then separated by fusing the glass constriction at 'b'. The γ-activity of the charcoal tubes and also of the frozen solution was then followed over a period of three days. Both tubes were placed in a holder close to the lead castle surrounding a Geiger tube of the type used previously, with constant geometry. Again following previous procedure, the solution, which was kept frozen to prevent changes in geometry due to emanation of radon, was placed

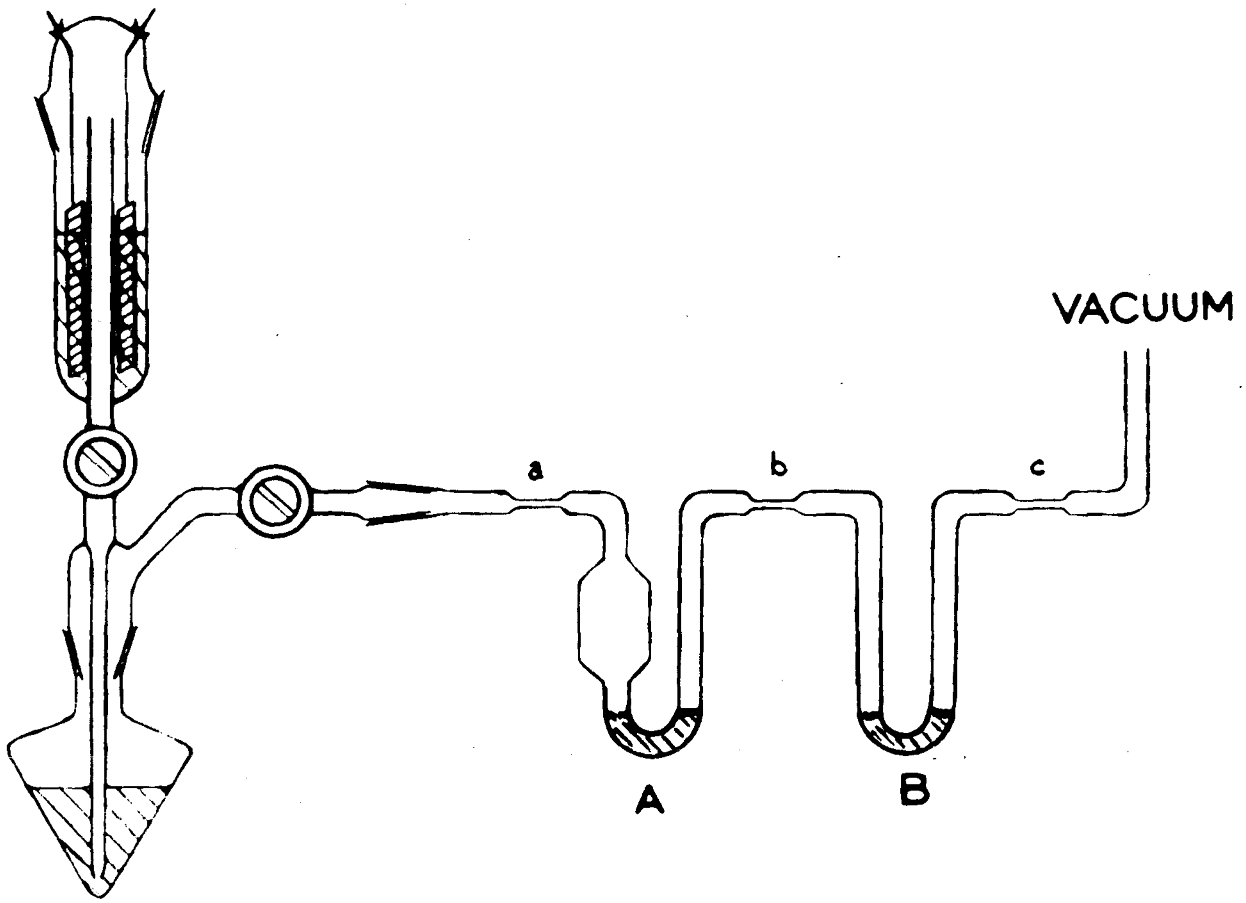


FIGURE 13

some distance from the counter. A uranium oxide standard was counted before and after each series of measurements to check on any variation in the characteristics of the counter or scaler; no corrections were necessary due to such errors. The collected results are given in Table 13.

TABLE 13

Decay of activity absorbed on charcoal, and growth of activity in degassed radium chloride solution

Radium Chloride Solution		Charcoal A		Charcoal B	
Time (hrs.)	Activity (c.p.m.)	Time (hrs.)	Activity (c.p.m.)	Time (hrs.)	Activity (c.p.m.)
0.25	876	3.42	1370	19.0	26800
2.84	873	4.17	859	27.25	25000
4.58	897	4.88	664	42.84	22650
19.08	1182	17.96	495		
23.25	1286	18.73	475		
27.58	1346	22.18	463		
42.70	1567	27.33	454		
47.45	1634	43.00	389		
66.40	1935	47.62	383		
		66.82	329		

The activity of charcoal B was so high as to cause difficulty in counting, after allowing time for the active deposit to come to equilibrium. The three values obtained when plotted logarithmically against time lie almost exactly on a straight line from which a half-life of approximately 4 days is deduced. Allowing for the inherent inaccuracies of the experiment this is in

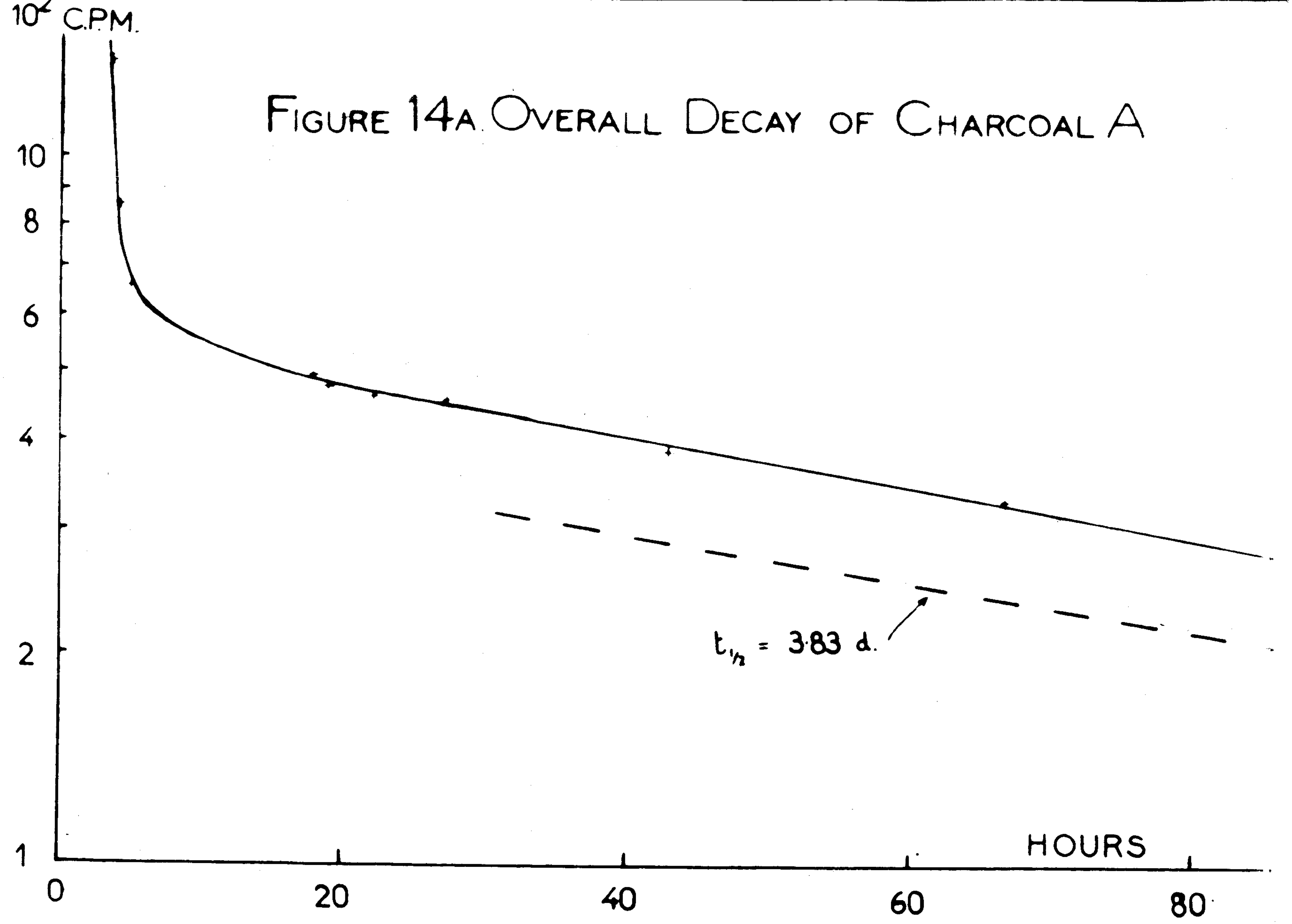


FIGURE 14A OVERALL DECAY OF CHARCOAL A

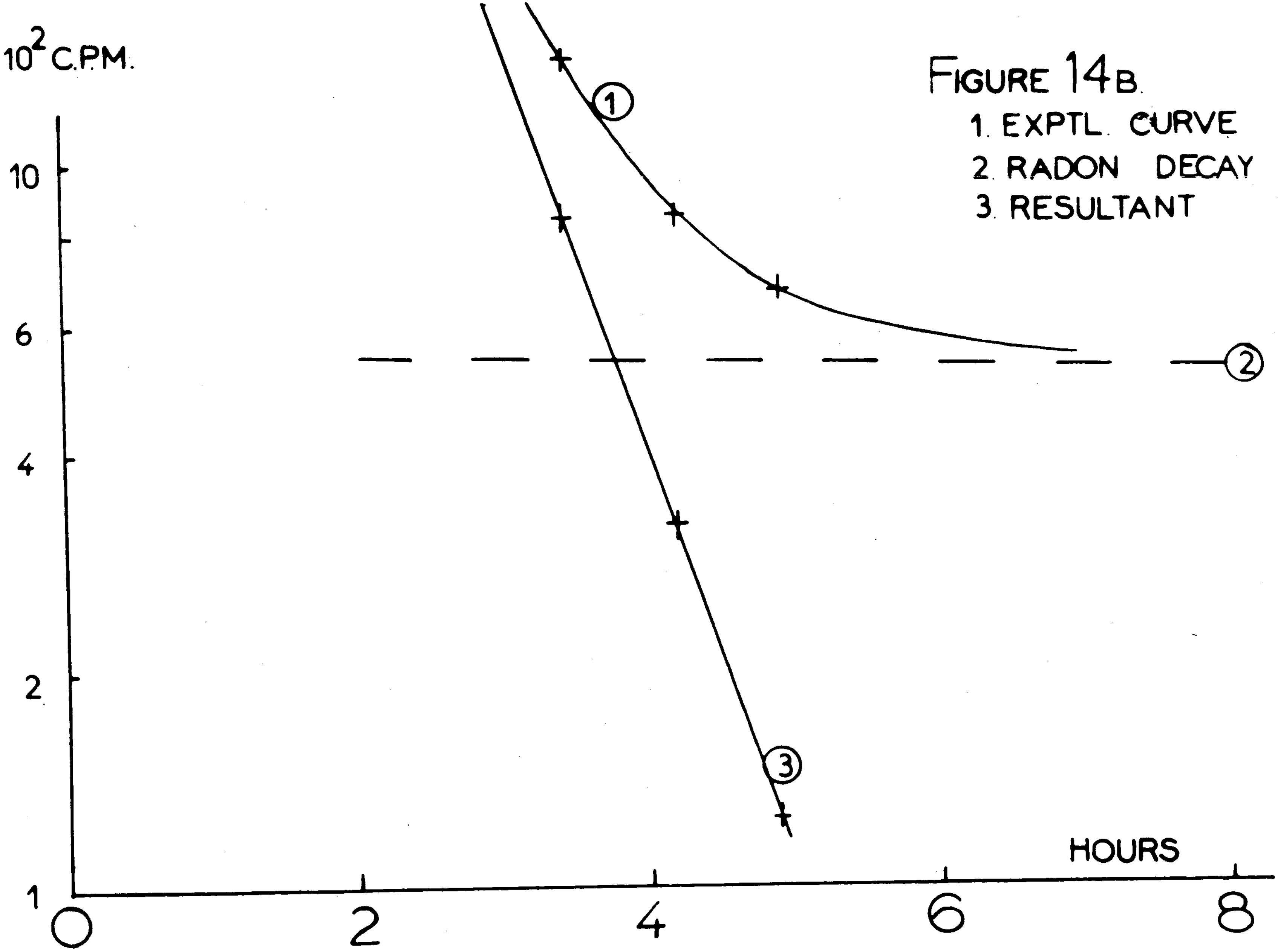
10² C.P.M.
10
6
4
2
1
0
2
4
6
8
HOURS
①
②
③
1. EXPTL. CURVE
2. RADON DECAY
3. RESULTANT

FIGURE 14B.

good agreement with the known half-life of radon. The decay of the activity in charcoal A shows a complex curve (see Figure 14) which can be resolved into two straight lines. The longer-lived activity is clearly radon, there being excellent agreement with the established half-life. The presence of radon in this tube may be due in part to interference with distillation from the water present, as mentioned previously. A comparison of the activities of tubes A and B after the short-lived activity of the former had died away almost completely (e.g. $t = 40$ hours) showed that about 2 per cent of the radon had been retained in A. By extrapolation, the short-lived activity in A was shown to have a half-life of 30 minutes, to be compared with the figure of 25.2 minutes calculated.

These experiments confirmed the radiochemical purity of the solutions and at the same time provided a significant clue inasmuch as it was shown that after $5\frac{1}{4}$ hours out-gassing, the solution of radium chloride still had a high γ-activity. Calculations (Section IIId) showed that after such a period, the γ-activity should be 0.2 per cent of the initial value. Both solutions of radium chloride were at radioactive equilibrium before this experiment, so that by measuring the γ-activity of the 1.01 mgm. solution immediately after the initial measurement on the outgassed 8.24 mg. solution, one was able to show that 23.5 per cent of the equilibrium γ-activity remained. This surprising result was ascribed to adsorption of radon on solid matter which had become visible in both solutions. The nature and genesis of this material is discussed later.

This phenomenon explains both the anomalous results on the γ-activity of the two solutions and the variation of helium yield with time. In the

γ-ray measurements, the weaker solution contained more radon than one calculated by assuming absence of radon at zero time and consequently the corrections applied for the growth to equilibrium were invalid. As equilibrium was approached, the errors involved became less important and so the theoretical ratio of the γ-activities was more and more closely approached. Since radon was closely held on the amorphous solid during the out-gassing of the solution, the additional α-particles from radon and its short-lived daughters provided helium not accounted for in the formulae deduced earlier. Helium, of course, will not be adsorbed at all by the material. A similar type of behaviour has been observed by E. R. Mercer; solutions of radium extracted from meteorites and minerals for age determinations gave low radon values if the solution from which the gas was being removed showed any turbidity.

IIIh. Experiments with Radium Bromide Solution

Whilst the investigation described above was under way, a solution of radium bromide was delivered from the Radiochemical Centre. It was decided to use this source, which contained 3 mg. of radium by γ-calibration, to check the performance of the helium apparatus. The first experiment gave a specific activity of $3.80 \times 10^{10} \alpha$/sec./gm. confirming clearly that no errors had arisen in the actual measurement of the gas. This solution was then allowed to stand at room temperature for four weeks, when the experiments were resumed. Three determinations carried out all showed high helium yields (see Table 14) and in fact visual examination showed the presence of traces of solid matter which had formed in the solution during the storage period. No further helium experiments were performed with this solution.

TABLE 14

Radium bromide solution : helium production

Strength : 3 mg. radium

	Time (hrs.)	Volume of He (ccs. x 10^6)	He from Ra alone (ccs. x 10^8/hr)	Time after transference (Days)
1	20.42	0.376	1.52	2
2	47.10	1.19	1.73	30
3	19.33	0.391	1.69	32
4	67.42	1.74	1.73	39

IIIh. Further Experiments with Radium Chloride Solutions

In view of the results obtained with the radium bromide solution, a similar series was carried out using a fraction of the 8.24 mg. solution of radium chloride. Approximately one third of this solution was removed, freed from solid matter by centrifuging and the clear solution placed in a new bubbler. The strength of this source was not known whilst the experiments were carried out, but later it was sealed and the daughter elements allowed to grow to equilibrium. Comparison was then made of its γ-activity with other solutions and also a calibrated standard, and a value of 2.3 mg. radium obtained. This figure is probably subject to an uncertainty of 5 per cent.

In each experiment a measurement of the γ-activity of the solution was made at the end of the 5 hour out-gassing period. The first measurement showed that with a clear solution the γ-activity fell to such a level as to be indistinguishable from the background of the counter. The first five results shown in Table 15 were obtained within 20 days of the purification of the solution and show excellent agreement. In no case was there any significant γ-activity after the initial out-gassing of the solution. A fortnight then elapsed and two further experiments were performed: in each experiment, high helium yields were found, agreeing with the retention of approximately 3-5 per cent of the γ-activity at the beginning of the accumulating period. As with other experiments with γ-calibrated solutions, no absolute significance can be attached to the results.

TABLE 15

Radium chloride solution, cleaned by centrifugation : helium production

	Time (hrs.)	Volume of He (ccs. x 10^6)	He from Ra alone (ccs. x 10^8/hr.)
1	66.75	1.29	1.18
2	42.60	0.744	1.23
3	67.08	1.30	1.21
4	42.67	0.765	1.26
5	42.58	0.767	1.26
6	19.00	0.312	1.37
7	19.08	0.304	1.33

IIIj. The use of Solid Radium Preparations; Preliminary Experiments

When it was realised that the estimation of the specific α-activity of radium using solutions had certain apparently inherent difficulties, it was decided to investigate the alternative of using a solid. There is, of course, a precedent for this in the work of Boltwood and Rutherford[10] described earlier.

Preliminary investigations on the de-emanation of such a source were carried out on a tracer scale. To 2 ml. of 1N. barium chloride solutions was added 1 ml. of a solution of radium chloride containing 4 μc/ml. of radium. Sulphuric acid was added dropwise, the solution warmed for five minutes on a water bath and the precipitate centrifuged out and washed twice with water. The precipitate was then slurried and transferred pipette-wise to a nickel tube containing 0.5 gm. of fusion mixture. This was dried, a further quantity of fusion mixture added and the whole fused over a Meker burner. The heating was continued for twenty minutes; on cooling, a clear solid was obtained. This source was then sealed in a specimen tube and the active deposit allowed to grow to equilibrium.

A second, identical, source was also prepared and heated under vacuum in the apparatus shown in Figure 15A. After 5 hours at red heat, the γ-activity of this source was still appreciable. Since radium itself emits weak γ-rays, the γ-ray absorption spectrum of the first source, now nearly at equilibrium, was investigated, using the experimental set-up recommended by Friedlander and Kennedy[36]. Lead absorbers, of various thickness, were placed over the source, which was 5 cm. below the window of a bell-type Geiger tube; a thin layer of aluminium (1.14 gm. cm.$^{-2}$) was placed immediately below this window to cut out bremstrahlung. The results obtained are given in Table 16A and plotted semi-logarithmically in Figure 16. The earlier part of the curve, relating to the weak γ-rays from radium, is unfortunately not clear. For the straight-line portion of the graph one derives a half-thickness of 15.9 gm.cm.$^{-2}$, in good agreement with the values deduced from the review by Glendenin[37], for radium-C γ-rays (1.8 Mev, $\mu_{\frac{1}{2}}$ 15.1 gm.cm.$^{-2}$, with 0.6 per cent 2.2 Mev, $\mu_{\frac{1}{2}}$ 16.1 gm.cm.$^{-2}$)

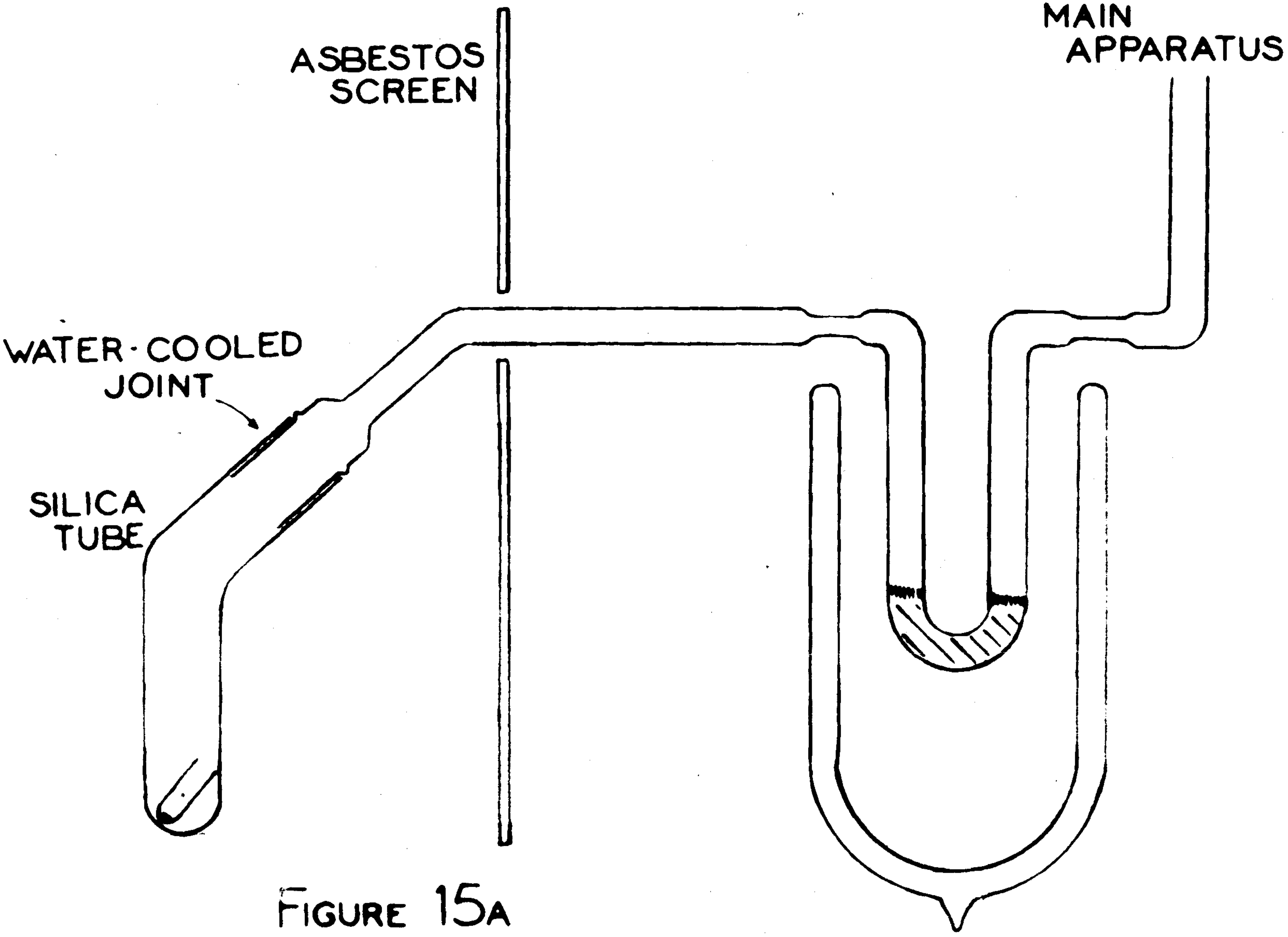

ASBESTOS SCREEN
MAIN APPARATUS
WATER-COOLED JOINT
SILICA TUBE

FIGURE 15A

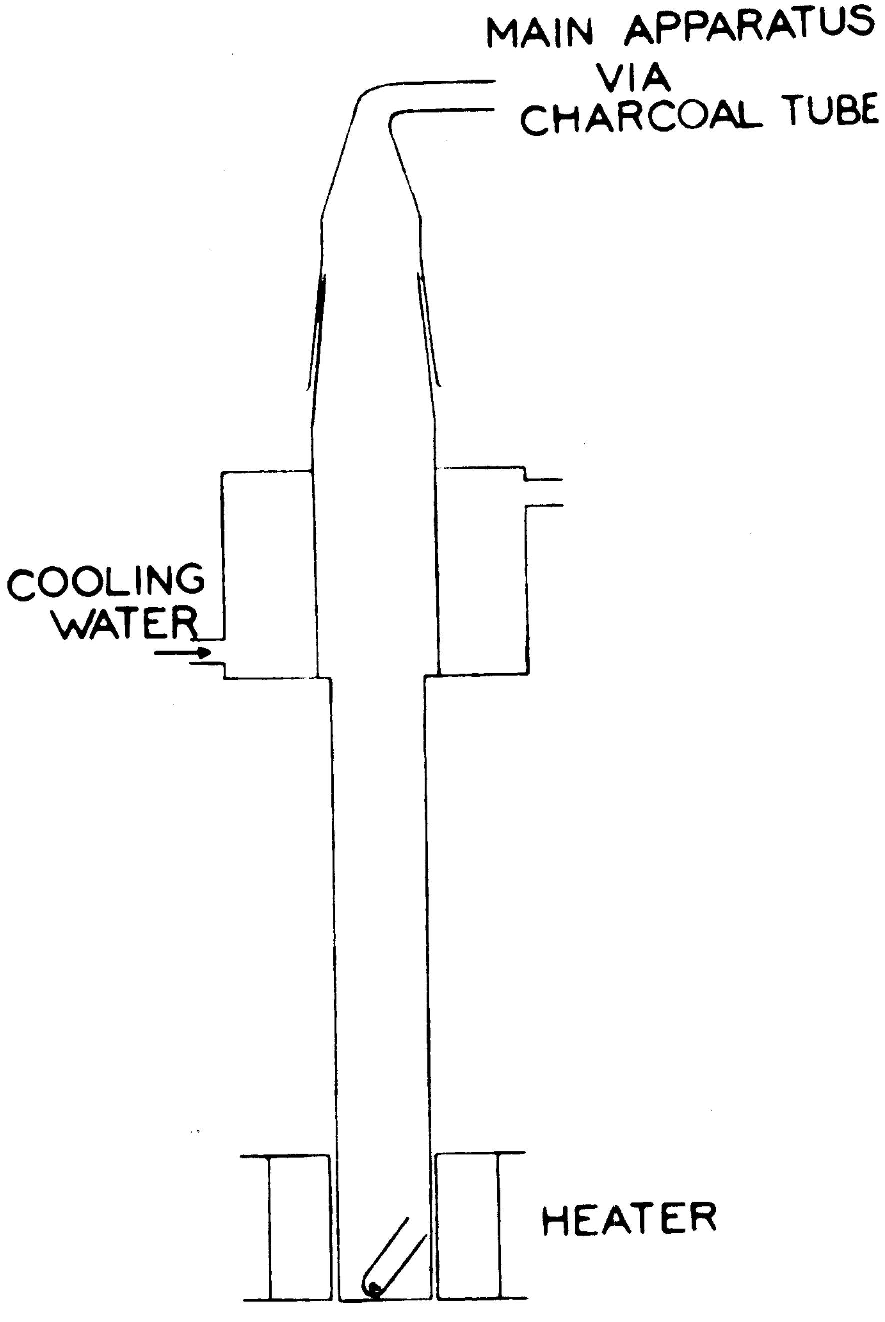


FIGURE 15B

TABLE 16

γ-ray absorption measurements on 4 μc. source of radium sulphate

A. Lead absorber gm. cm.$^{-2}$	0	2	4	6	8	10
c.p.m.	823	650	607	557	499	469
B. After out-gassing procedure Lead absorber gm. cm.$^{-2}$	0	2	4	6	8	10
c.p.m.	138	127	92	73	75	68

The absorption measurements were repeated on a source after 5 hours heating in the apparatus used previously. Results are shown in Table 16A and graphically in Figure 16; again the RaC γ-rays are clearly identified. By comparing the radium-C γ-activity extrapolated from the graphs, one found that only 86 per cent of the radon had been removed by the heating. In view of the absorption measurements, it was decided to make all γ-determinations using a lead absorber to cut out completely the γ-rays from radium. The absorber actually used had a thickness of 3.8 gm.cm.$^{-2}$.

It was thought that the poor de-emanation achieved was due to the poor thermal transmission of silica resulting in local region of comparatively low temperature in the fused salt. A new heating apparatus was constructed of metal with facilities for electrical heating of the lower region. This is shown in Figure 15B. Using this set-up, the RaC γ-activity was reduced from 2300 c.p.m. to approximately 4 c.p.m. after $5\frac{1}{4}$ hours heating. This remaining

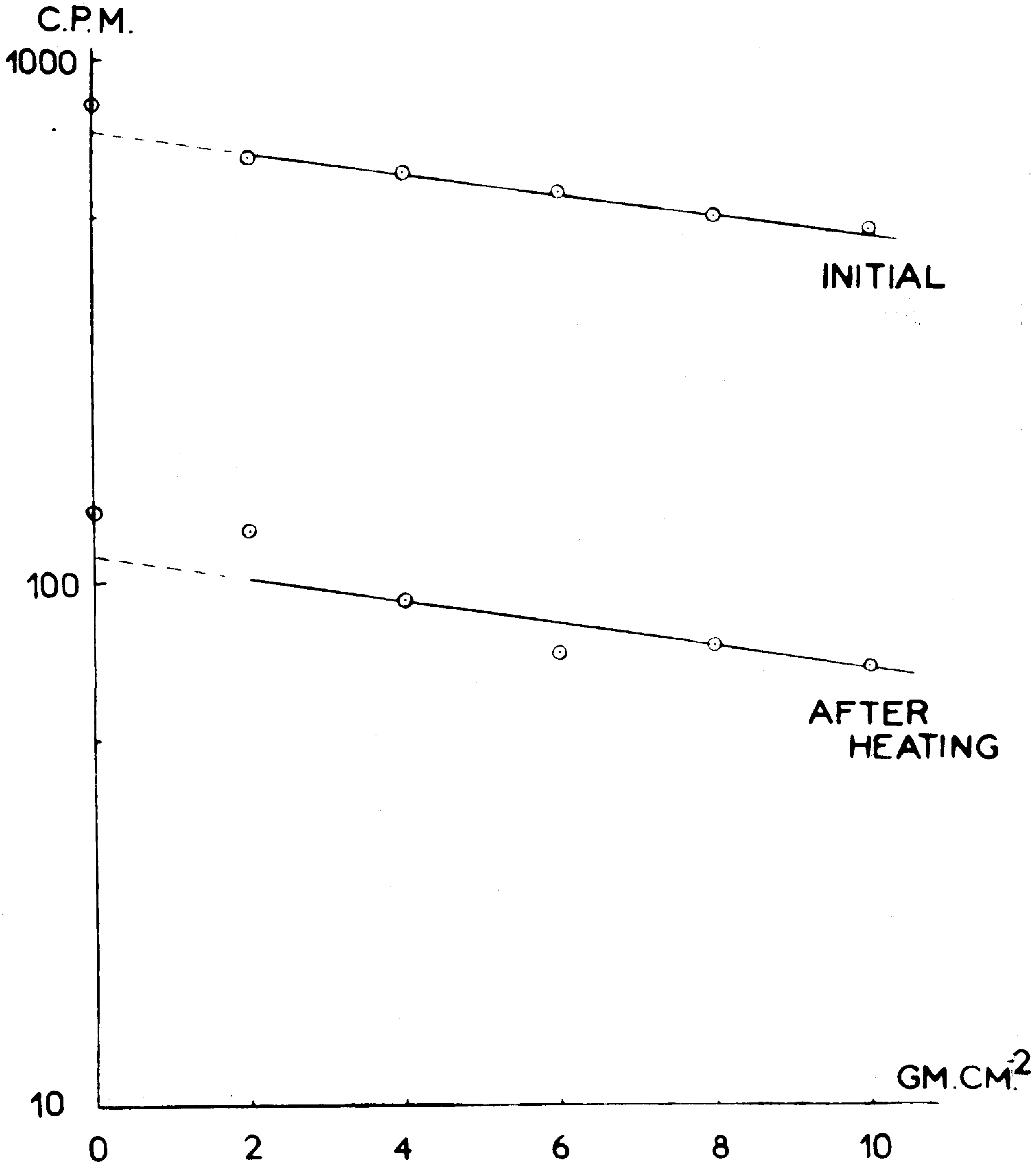


FIGURE 16

activity is that to be expected (see Section IIId). In view of this result, which was confirmed by a further experiment on a similar source, it was decided to carry out experiments on a scale permitting of helium measurements.

IIIk. Helium Yields from a Solid Radium Preparation

For these experiments, the solution of radium bromide previously used was converted to the insoluble sulphate. This solution and the residue formed in it by the action of its radiations on the soda-glass vessel were transferred to a centrifuge tube, almost neutralised with ammonia and excess dilute sulphuric acid added. The supernatant liquor was removed. After centrifuging and twice washing the precipitate, it was slurried and transferred to a steel tube containing 1 gm. of fusion mixture, and the mixture warmed gently to dry it. Stronger heat was then applied to fuse the mixture which was transferred to the apparatus previously used (Figure 15B) after cooling. It was realised that the separation procedure used may not have resulted in quantitative transfer of radium, due to the difficulties involved in the precipitation of radium sulphate in the absence of a carrier. However, since these experiments were intended to be exploratory, this was temporarily ignored.

In the event, the results obtained were of poor quality due to the behaviour of the Pirani gauges. This defied all efforts to achieve favourable conditions for measurements despite the time spent on this (see Section IIf). The results of those experiments carried to completion are given in Table 17. No modification to the experimental procedure previously used was necessary; since no carrier gas was used, no enlargement of the bore of the charcoal U-tube was necessary during the five hour out-gassing period. In each case, the γ-activity was checked after the de-emanation and found to have fallen to negligible proportions. In view of the difficulties under which the experiments were carried out, the internal agreement of the results is fairly satisfactory.

TABLE 17

Solid source of radium sulphate : helium production

	Time (hrs.)	Volume of He (ccs. x 10^6)	He from Ra alone (ccs. x 10^8/hr.)
1	93.5	1.74	1.16
2	66.92	1.05	0.96
3	43.00	0.84	1.37
4	43.42	0.84	1.34
5	43.92	0.76	1.20 Average value 1.21 ± 0.10

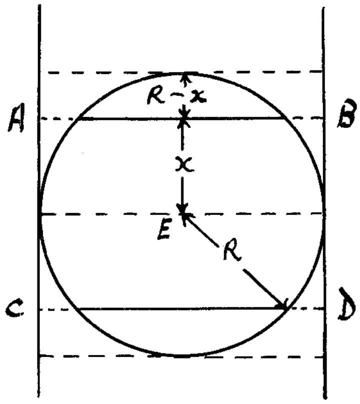
IIIl. Loss of Alpha Particles in a Generating Solid

In the type of experiment where one wishes to collect and measure the amount of helium generated in a solid source, it is necessary to consider the losses due to absorption of α-particles into the walls of the containers. Such α-particles will, in general, not be collected for measurement. A similar calculation for solutions is not necessary, since the volume of solution per milligram of radium was of the order of 5 cc./mgm; as is shown below, this is approximately ten times higher than was the case for a solid source.

Consider the example, of a pure radium salt, of weight 'w' and density ρ. For simplicity of calculation, we shall consider the source to be spherical in shape, although this is, in fact, the most favourable case for minimum losses, since a sphere has the minimum surface area per unit volume.

It then follows that the volume, V, is given by $w/\rho = 4/3\ \pi\ r^3$. So that 'r', the radius of this sphere is given by $r = \sqrt[3]{\frac{w}{\rho} \cdot \frac{3}{4\pi}}$

If the range of the α-particles in the medium in question is R (equivalent to a range of R_1 cm. in air), it can be shown that 25 per cent of the α-particles arising within a volume segment of depth R cm. from the surface will not be collected for measurement. (In the equivalent calculation considering the loss of α-particles before entering say, an α-counter, one must make a further allowance for the energy dissipated in traversing the air gap between surface and counter and the window of the counting tube itself). Consider a sphere with particles originating from the centre, traversing a plane at AB.



The plane CD is a distance R from AB. Then the fraction of the total number of α-particles originating at E which escape from the volume ABCD across AB, will be the ratio of the appropriate surfaces of the sphere. These can be simply written as the ratio of the corresponding surfaces of the circumscribing cylinder

$$= \frac{R - x}{2R}$$

Integration of this within the limits x = o, x = R, gives the total number escaping

$$= \int_{o}^{R} \frac{R - x}{2R}\ dx$$

and the fraction lost will be

$$\int_0^R \frac{R - x}{2R} \cdot \quad dx$$

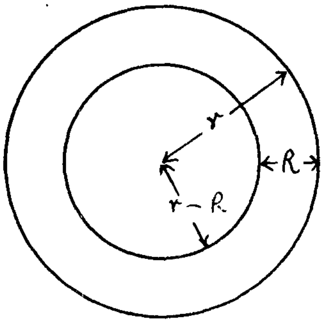
$$= \frac{1}{R}\left[\frac{1}{2} \cdot x - \frac{x^2}{4R}\right]_0^R$$

$$= \frac{1}{R}\left[\frac{R}{2} - \frac{R}{4}\right]$$

$$= 1/4$$

i.e. percentage loss = 25 per cent.

Now in the sphere of α-emitting material of radius r, we can consider the outer volume segment of depth R from which α-particles may be lost. This volume is given by



$$\frac{4}{3}\pi r^3 - \frac{4}{3}\pi (r - R)^3$$

$$= \frac{4}{3}\pi\left[r^3 - r^3 + 3r^2R - 3rR^2 - R^3\right]$$

We shall ignore terms involving powers of R greater than unity, and hence the segment has a volume $4/3 . \pi \left[3r^2R\right] = 4\pi r^2R.$

Remembering that the percentage loss is 25 per cent in any segment of depth R, the total percentage loss is

$$\frac{4\pi r^2R}{4/3 . \pi r^3} \cdot 25$$

$$= \frac{3R}{4r} . 100$$

The ranges of α-particles are usually given for "standard air" (dry air at 760 mm. pressure and 15°C.). For materials other than air, the range depends on the density of the medium and on its atomic composition. The exact form which this dependance takes is somewhat obscure and for practical purposes one can use the "atomic stopping power(s)" for normal α-particle energies. Very roughly

$$S \propto \sqrt{A}$$

or, to a better approximation

$$S = 0.563 \left[\frac{Z}{(Z + 10)^{\frac{1}{2}}} \right]$$

where A = atomic weight, Z = atomic number.

This is, of course, a purely empirical formula, with the factor 0.563 introduced to make $S_{air} = 1$. The molecular stopping power is taken as the sum of the stopping powers of the constituent atoms; this would be invalid for accurate work since the distribution of the energy losses differs for different atoms[37]. However, for the problem under consideration it is certainly accurate enough.

For an elementary material

$$R = R_{air} \times \frac{(\rho_{air})}{(M_{air})} \times \frac{A}{\rho . S}$$

$$= R_{air} \times \frac{0.001226}{14.4} \times \frac{A}{\rho . S}$$

and for a non-elementary material

$$R = R_{air} \times 8.5 \times 10^{-5} \times \frac{M}{\rho S}$$

This gives a method whereby one can calculate the losses from any solid source experiment. We shall consider firstly the experiment of Boltwood and Rutherford, who used a $RaCl_2/BaCl_2$ mixture containing 7 per cent of radium. This is somewhat ambiguous, but most likely means that 7 per cent of the $RaCl_2/BaCl_2$ is radium chloride. Since, by γ-ray measurements, the salt contained 192 mgm. of radium, the total weight of $RaCl_2$ is $192 \times \frac{384}{226} = 0.326$ gm.

Hence, the total weight of salt is 3.75 gm. (approx.).

For the elements Ra, Ba and Br, one calculates atomic stopping powers of 5.01, 3.87 and 3.22 respectively, so that $\sum s$ for this particular source is

$$2 \times 3.22 \quad \times \frac{7 \times 5.01 \times 93 \times 3.87}{100} \quad = 10.39$$

For this source, the average molecular weight is 301.2 and the density 4.85. There are four α-emitters involved, each with complex spectra, so that the best approximation is put $R_{air} = 5$ cms.

Then R_2, the range in the solid salt

$$= \frac{5 \times 8.5 \times 10^{-5} \times 301.2}{4.85 \times 10.39}$$

$$= 2.56 \times 10^{-3} \text{ cms.}$$

Now for 3.75 gm. of solid, assuming spherical form,

$$r = \sqrt[3]{\frac{3 \times 3.75}{4 \times 4.85}} = \sqrt[3]{0.134}$$

$$= 0.51 \text{ cm.}$$

Therefore, loss of α-particles

$$= \frac{3 \times 2.56 \times 10^{-3} \times 100}{0.51 \times 4}$$

$$= 0.32 \text{ per cent}$$

In the experiments described in this thesis, the source of 3 mgm. Ra as $RaSO_4$ was diluted with 2 gms. of fusion mixture for the express purpose of reducing the α-particle loss into the containers. For such a mixture, neglecting the $RaSO_4$, one calculates

$$M_{air} = 117$$

$$s = 6.93$$

$$\rho = 2.76 \text{ gms./cm.}^3$$

So that

$$R_2 = 5 \times 8.5 \times 10^{-5} \, \frac{\times 117}{6.93 \times 2.76}$$

$$\doteqdot 2.60 \times 10^{-3} \text{ cm.}$$

For a total weight of 2.3 gm. and density 2.76,

$$r = 0.58 \text{ cm.}$$

Therefore loss of α-particles = 0.34 per cent.

CHAPTER IV. DISCUSSION

IVa. The Effect of Ionising Radiations on Soda Glass

The development of an amorphous flocculent solid in the soda-glass vessels used as containers for the $RaCl_2$ used in the early series of experiments was noted previously. The obviously erroneous results obtained were ascribed to adsorption of radium on this solid with consequent falsification of the assumptions made concerning removal of radon and the active deposit. The experiments described below were directed towards the elucidation of the nature of this absorbent and the mechanism of its formation.

The solid itself was of an amorphous flocculent nature, yellow to white in colour (apparently depending on its history) and denser than the solution. One suspected this as the cause of the errors when high γ-activities were found in solutions of $RaCl_2$ which had been degassed for 5 hours. In a typical example of this type, 23 per cent of the γ-activity remained. A sample of this solid matter was therefore removed from one of the solutions and after thorough washing, sealed and tested for γ-activity; the approximate constancy of the activity found showed an adsorbate of radium and not radon. This counting was carried out as previously with the source approximately 1 metre away from a Geiger tube in a lead castle.

TABLE 18

Time after sealing (hrs.)	4.5	19.5	44.5
Activity (c.p.m.)	1008	1050	1099

The slight increase in activity is due to the comparatively slow growth of radon and the active deposit to equilibrium with radium; clearly, if the adsorbed element were radon, one would have found a fall in γ-activity in this time. The γ-activity of this adsorbate was approximately 20 per cent of the total activity of the solution from which it was extracted. This is in good agreement with the figure of 23 per cent given above; apart from any removal of adsorbed material in the washing process, errors are to be expected because of the different geometry of the two sources, since one was a solid of small volume and the other a larger bulk of liquid.

The vessel which had contained this solution was thoroughly cleaned and washed; the inner surface was observed to be strongly etched. This etching was not affected by inorganic acids (conc. HCl, dil. HCl, HNO_3), organic solvents (benzene, carbon tetrachloride) or boiling water. The glass itself had the brown colouration characteristic of γ- or X-ray action; this disappeared slowly on heating the vessel on a steam bath over some days.

The amorphous solid material was of such a physical nature as to suggest that it originated from breakdown of the glass and had not arisen from grease on the ground joints and taps associated with the system. This view was confirmed when a large amount of flocculent white precipitate appeared in a stoppered soda-glass container of the usual design, after it had been used for storing a solution of 3 mgm. radium chloride for 8 months in the complete absence of grease of any sort. This last sample of precipitate was much lighter in colour than those previously observed. A rapid production of the solid was found when, in the course of some later work, an attempt was made to concentrate by evaporation a solution of $RaCl_2$, cleaned by centrifugation, in a soda-glass container. The poor quality of the glass from a chemical point of view was demonstrated when, after maintaining an acidic solution of $BaCl_2$ (in 2N. HCl) on a steam bath without actual boiling for a fortnight, slight traces of a white substance, presumably silica, were observed. The quantity produced was extremely small and was not comparable with the amounts observed in the previous cases. A fresh soda-glass vessel containing a similar acid solution of $BaCl_2$ subjected to the γ-radiation from a 1.2 c. Ra source showed such exceedingly minute quantities of deposit as to cause doubt as to its nature, while in the same time the glass had noticeably coloured. In all experiments, precautions were taken against contamination of the solution by dust. Little chemical work was done on the material produced in the vessels containing solutions of radium salts; it was shown to be insoluble in mineral acids (HCl, HNO_3), and not noticeably affected by temperatures up to 100°C.

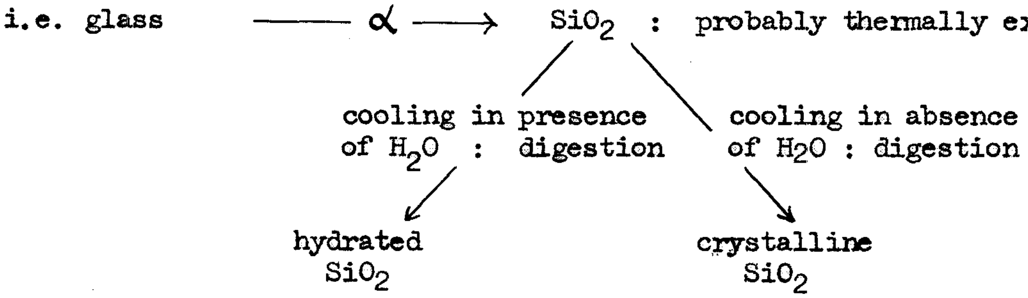
In general, the effect of ionising radiations on glasses of various types presents some curious results. The colouring produced by γ- and X-rays (noted in our soda-glass containers as a brown colour) and the fluorescence observed on destruction of this colouration by heating, has been investigated by many workers[38]. This phenomenon is now attributed to the formation of colour centres; previously, explanations of a purely chemical type had been presented[39]. Froudel[40] has shown that there are also effects of a physico-chemical nature in silica such as changes in elastic constants and in the rate of dissolution in hydrofluoric acid. Experiments with radon in silica showed rapid initial changes due to α- and β-particle action and a slower change due to γ-rays. A shallow region of intense colouring, with a change in refractive index on the inner surface of a glass tube which had contained radon was reported by

	Vessel	Original Contents	Contents during digestion	Observation
1	Tube A	0.5c. Rn	10 mls. H_2O	Formation of deposit of crystalline appearance
2	Tube B	0.5c. Rn 10 mls. dil. HCl	HCl removed to test tube and replaced by 10 mls. H_2O	Formation of a deposit of an amorphous type.
3	Test-tube	-	dil. HCl from Tube B	No deposit.
4	Test-tube	-	Small quantity of dil. HCl from Tube B plus few mls. dil. $BaCl_2$ solution.	No deposit.

No quantitative data were obtained, although it did appear that more deposit was formed from the tube irradiated in the presence of HCl. If this is so, one is led to assume that the production of solid is much more efficient in terms of α-particle input since the number of α's striking unit area is obviously smaller in this case due to the greater density of the medium.

A theoretical discussion of the disordering of solids by massive particles has been presented by Seitz[43], taking account of loss of energy by elastic collisions and by excitation and ionisation of electrons. From the number of atoms ejected from the lattice by elastic collision, the relationship of the number of displacements to the energy input is deduced. On the assumption that 10 per cent displacement is necessary to change the physical properties of a solid, Seitz calculates that 10^{17} α-particles (of approximately 5 Mev energy) striking 1 cm.^{2} should produce discernible changes. Calculations show that in the case of the dry-way irradiation, the total dose received was approximately 5×10^{15} α/cm.^{2} and as noted above, this will be reduced for the liquid phase bombardment. It seems clear therefore that disordering of this type can have played little part in the breakdown of the glass surfaces.

The evidence available suggests that the rate of precipitation of the solid material in an α-active solution is governed by the rate of leaching by the liquid phase. This is extremely slow but increases rapidly with rising temperature. The exact mechanism of the changes which take place in the glass is uncertain and it is hoped to carry out further work on this problem in the future. Initially it was thought that the leaching was possibly due to radiochemical reactions in the liquid. Although the exact mechanisms involved in the radiation chemistry of water is still the subject of some discussion, it is generally agreed that the primary act involves the production of H and OH radicals. It is possible that the high degree of ionisation along the track of an α-particle emitted in the solution produces sufficient radicals to set up local regions of high reactivity. When this takes place near the surface of the glass, leaching of silica from the latter can take place: as these regions are dispersed by diffusion, precipitation of hydrated silica takes place, since the solution is acidic. It is clear, however, that although this type of reaction may play some part in the overall degradation scheme it cannot be the whole explanation, in view of the production of silica following dry-way bombardment. Some interaction in the solid phase causes modification of the structure of the glass and it seems possible that this change is due to the energy dissipated in a small region of the lattice by the stopping of the incident α-particle. If this is a valid mechanism, it would be comparable with the formation of silica, on the macro-scale, in molten glass by devitrification. One should note that although devitrification implies precipitation of crystalline silica, on the micro scale envisaged any crystallites formed would appear amorphous to X-ray examination. Both deposits discussed above were, in fact, amorphous to X-ray analysis. The theory suggested could explain the formation in the absence and presence of water.



However, until further experimental work has been carried out, no definite conclusions can be drawn.

IVb. The Results of the Various Helium Measurements

In view of the aim of the helium experiments described in Chapter III, and the importance of the radium specific activity in the field of radioactive standardisation, the results obtained are extremely disappointing. Neither main series of experiments yielded absolute values for the specific activity, since the amount of radium used was not known by any but a rather inaccurate comparative measurement. The results obtained in the later work with purified radium chloride (Section IIIh) show that with such a solution a series of internally consistent figures could be obtained. Independant calibration of this solution could have given the radium content much more accurately; this however, would not have yielded an absolute result for the specific activity but merely another in the series of values dependent upon γ-ray calibration.

With one exception, none of the difficulties encountered in this work can be considered as anything but "trivial" despite the time and effort necessary to overcome them. Many of the day-to-day breakdowns of the helium apparatus could be ascribed to the age of the apparatus; the recalibration of the pipetting system (Section IIh) and the difficulties with the Pirani gauges, whilst being extremely time-consuming, were not fundamental problems in the sense that they can be held to detract from the advantages of the helium method of α-particle measurement. The more serious problem of the formation of silica in the solution experiments is discussed below.

IVc. Recommendations for Further Work

The technique of helium measurement as used in these and other experiments in the Londonderry Laboratory for Radiochemistry does not appear to require any significant changes for future work. Much attention will have to be paid to the system used for radium storage and helium collection. The use of soda-glass vessels in conjunction with strong α-emitting solutions is clearly to be avoided. This problem could be overcome by the use of a metal vessel for the bubbler, but this may be rather undesirable experimentally. A possible modification would be to store the solution in a metal container, transferring it to a glass vessel only for the brief period of the actual experiment. Pyrex glass is known to be much more resistant to radiation damage than soda, which suggests that it might prove suitable for use in the construction of the bubbler. The diffusion of helium through the small surface area should be negligible within the time of an experiment especially since for most of this period the vessel is at -78°C. The problem of the initial degassing of the pyrex might prove to be a much more serious difficulty in such experiments. One tentative suggestion is to use a completely different type of solution such as that formed by the radium-TTA complex in an organic solvent. In the absence of water, the precipitation of hydrated silica is clearly prevented and as is suggested elsewhere, the decomposition of soda-glass appears to be less efficient in the absence of water. Many inert organic solvents (e.g. carbon tetrachloride) are much more stable towards radiolysis than is the case for water. At the same time, the technique of using a solid source of radium has many advantages of simplicity and cleanliness. It is not possible to argue from the results obtained that this type of experiment is uniquely preferable to the solution method; there is, however, no reason to suppose that had the helium apparatus functioned satisfactorily, an accurate series of results could not have been obtained. One general recommendation for future work is to use a wide variety of times and strengths of radium source to ensure that any time dependant factors are completely eliminated.

On the wider questions of radioactive standardisation, one would like to see the same radium preparation used as the starting point for several determinations by different methods. In this way, the assumptions made in these differing techniques could be critically examined and a generally acceptable value for the specific activity of radium should be obtained.

APPENDIX

THE THEORY OF THE PIRANI GAUGE

The early theory presented by Campbell[44] and his associates discusses the case of varied applied potential, with constant filament temperature for different gas pressures. The various heat losses from the filament wire (radiation, conduction along the supports and conduction in the gas) are all approximately proportional to the temperature difference between the filament and its surroundings ($= \theta$). Let the losses due to radiation, and conduction through the supports (which are independent of pressure) be $r\theta$, and let that due to gaseous conduction be $c.f(p)\theta$, where p is the gas pressure. The heat supplied to the wire, since the resistance of the bridge is always the same, is proportional to V^2, where V is the potential applied to the bridge.

Let the heat input be αV^2

Then $[r + c.f(p)]\theta = \alpha V^2$

If V_o is the potential applied at $p = 0$, $r\theta = \alpha V^2$, and

$$\frac{V^2 - V_o^2}{V_o^2} = \frac{c}{r} \cdot f(p)$$

c/r is constant, being independent of length, diameter and material (Pt or W); when θ, and changes of θ are so small that all heat losses are proportional to θ, the value of c/r does not change with temperature. If two gauges (of practically the same construction) are used in a bridge, $\frac{V^2 - V_o^2}{V_o^2}$ should be independant of everything except the nature and pressure of the gas. This was confirmed experimentally.

A theory which derives theoretically the relationship found experimentall by Campbell has been presented by Takamura[45]. We shall follow his reasoning so far.

Let p.d. across filament = V, resistance R.

Q_1 = dissipation of heat by conduction of gas

Q_2 = " " radiation

Q_3 = " " convection in gas

Q_4 = " " conduction through filament supports

Then $\frac{V^2}{R} = Q_1 + Q_2 + Q_3 + Q_4$

of these Q_3 and Q_4 will be negligible at low pressures. When the gas is at very low pressures one assumes throughout that the molecular free path is large compared with the diameter of the tube.

Now Takamura proceeds to assume that molecules striking the filament and the wall attain temperature equilibrium with them. He then writes

$$\frac{V^2}{R} = \frac{1}{6} ANm\bar{c} \cdot C_v(T_1 - T_2) + A\sigma(T_1^4 - T_2^4)$$

Where A = total filament area

N = number of molecules per cm.^{3}

m = mass of molecules

$\bar{c}$ = mean molecular velocity

C_v = molecular specific heat at constant volume

T_1 and T_2 = temperature of filament and container respectively

σ = radiation coefficient

From this, using an experimental method in which one balances voltage to keep the filament temperature constant at all gas pressures, he deduces

$$\frac{E^2 - E_o^2}{E_o^2} = kp \quad \text{(the Campbell equation).}$$

Now it is clear that Takamura is unjustified in assuming that molecules striking the filament and the wall attain temperature equilibrium with them. Many authors have shown that this is definitely not the case and that an 'accommodation coefficient' is necessary to cover the case where temperature equilibrium is not reached in single collisions.

Miller[46] deduces, for a monatomic gas striking a wire at temperature T_1 (gas temperature T_2), the loss of heat as

$$\frac{ap}{(2\pi mkT_2)^{\frac{1}{2}}} \cdot 2k(T_1 - T_2)$$

which can be written more simply as

$$1.74 \times 10^4 \frac{ap.(T1 - T2)}{(MT_2)^{\frac{1}{2}}} \quad \text{cals. sec.}^{-1} \text{ cm.}^{-2} \qquad (1)$$

where M is the molecular weight of the gas at a pressure of p dynes cm.$^{-2}$. The effect of non-equilibrium collisions of gas molecules with the wall of the containing vessel is ignored; this would result in only a small correction and would in any case not influence the final result, since only the absolute value of T_2 is affected.

We can replace Q_1 in Takamura's equation with expression (1) and write

$$\frac{E^2}{R} = A\left[1.74 \times 10^4 \cdot \frac{ap\ (T_1 - T_2)}{(MT_2)^{\frac{1}{2}}} + \sigma\,(T_1{}^4 - T_2{}^4)\right]$$

The accommodation coefficient is constant for like measurements on the same gas. As before, we can put $E = E_o$ at $p = 0$, and deduce the Campbell formula.

Thus there is no first order of dependence of power input on resistance, so that to a first approximation, W is constant. It follows that the temperature of the filament must so adjust itself with pressure changes so that the increased conduction losses in the gas are balanced by reduced radiation losses.

Suppose T changes to T - Δ T

Then R = α RΔT where α is the temperature coefficient of the filament material.

As before

$$\frac{E^2}{R} = \frac{1.74 \times 10^4 \, a.A.p}{(MT_2)^{\frac{1}{2}}} (T_1 - T_2) + A\sigma\left[T_1^4 - T_2^4\right]$$

and $W_{p=0} = W_{p=\delta p}$

So that

$$\frac{1.74 \times 10^4 \, a.A.}{(MT_2)^{\frac{1}{2}}} \delta p \, . \, (T_1 - \Delta T - T_2) + A\sigma\left[(T_1 - \Delta T)^4 - T_2^4\right]$$

$$= W = A\sigma . (T_1^4 - T_2^4)$$

We can expand the fourth power terms, cancel T_1^4 and T_2^4 and neglect terms involving ΔT to powers higher than unity. Furthermore, since ΔT is negligible compared with T_1 and T_2, we can put

$$T_1 - T_2 = T_1 - \Delta T - T_2$$

i.e. $$\frac{1.74 \times 10^4 \, a.A.}{(MT_2)^{\frac{1}{2}}} \delta p \, (T_1 - \Delta T - T_2) = A\sigma\left[4T_1^3 . \Delta T\right]$$

whence $$\frac{1.74 \times 10^4 \, a.}{(MT_2)^{\frac{1}{2}}} \delta p \, . \, \frac{(T_1 - T_2)}{4T_1^3\sigma} = \Delta T$$

The scale of the galvo has been corrected for non-linearity and so deflections on it are directly proportional to ΔR, and thus to ΔT and hence δp for samples of the same gas. This is only true of course, when the pressure is sufficiently small to allow the assumption of the condition stated by Miller regarding the conduction of heat by a gas. From the last formula, we can derive a condition for change of filament temperature with pressure

i.e. $$\frac{\Delta T}{\delta p} = \frac{1.74 \times 10^4 \, a \, (T_1 - T_2)}{(MT_2)^{\frac{1}{2}} \quad 4\sigma T_1^3}$$

and since, as previously noted

$$\Delta R = \alpha R . \Delta T$$

$$\frac{\Delta R/R}{\delta p} = \frac{\alpha a \; 1.74 \times 10^4 \, (T_1 - T_2)}{(MT_2)^{\frac{1}{2}} . \; 4\sigma T_1^3}$$

so that $$\frac{V}{R} . \frac{\Delta R}{\delta p} = \frac{V \alpha a \; 1.74 \times 10^4 \, (T_1 - T_2)}{(MT_2)^{\frac{1}{2}} . \; 4\sigma T_1^3} \qquad (2)$$

Now at zero pressure the radiation losses constitute the balancing factor for the power input

$$W = V^2 R \propto \sigma (T_1^4 - T_2^4)$$

i.e. $$V = K_1 (T_1^4 - T_2^4)^{\frac{1}{2}}$$

Substituting this into the right hand side of equation (2) and simplifying

$$\frac{V}{R} . \frac{\Delta R}{\delta p} = K_2 . \frac{(T_1 - T_2)\,(T_1^4 - T_2^4)^{\frac{1}{2}}}{T_2^{\frac{1}{2}} . \; T_1^3}$$

Since the current flowing the galvanometer and its shunt resistance is proportional to $V.\Delta R/R$, the maximum value of this expression will give the optimum conditions. Writing S for the sensitivity of the system, in terms of galvanometer deflection per unit quantity of gas, one has

$$S \propto \frac{(T_1 - T_2)\ (T_1{}^4 - T_2{}^4)^{\frac{1}{2}}}{T_2^{\frac{1}{2}}\ .\ T_1{}^3}$$

Clearly for optimum sensitivity, $(T_1 - T_2)$ must be a maximum. However, if T_1 is greater than T_2,

$$S \propto \frac{T_1{}^3}{T_2^{\frac{1}{2}}\ .\ T_1{}^3} \qquad (3)$$

Since T_2 occurs only in the denominator, it must have a minimum value and this is achieved in practice by immersing the gauges in liquid nitrogen. The temperature of the filament does not affect S if the premises of equation (3) are true. In fact, however, if sensitivity is plotted against applied voltage, a maximum appears in the region of one volt, which consequently is the normal applied voltage. This implies that beyond certain filament temperatures, heat losses by conduction through the metallic filament supports are no longer negligible and eventually are so great that the sensitivity of the gauge falls off with increasing power input.

One further point to be noted from equation (2) is that, clearly,

$$S \propto \frac{a . \alpha}{\sigma}$$

which yields a method of comparing efficiencies of various metals for filament materials.

One difficulty implicit in this is that of obtaining reliable results for the accommodation coefficients. Some of the figures reported are shown in Table 19, and it is obvious that the experimental value of 'a' depends on the metal surface, its condition and its previous history. Thus the values for thoroughly outgassed surfaces are very different from those surfaces carrying a layer of adsorbed gas atoms or molecules. In the theoretical discussion of the question, Jackson and Howarth[47] have presented a wave-mechanical picture of the collision process (a classical mechanical theory was put forward earlier by Baule[48]). For the case of helium and tungsten, the effect of the impact of the helium atom on the vibrational modes of the tungsten lattice was calculated and agreement obtained with the results obtained experimentally by Roberts[49]. A further extension of the theory by Devonshire[50], to include the potential energy terms due to attraction between gaseous atom and lattice at larger distances allowed the case of neon on tungsten to be calculated.

TABLE 19

Accommodation Coefficients for Various Metals
(from Kennard, 'Kinetic Theory of Gases', McGraw-Hill, p.323)

Element	a_{He}	Conditions
Platinum	0.38	
	0.50	
	0.44	Bright platinum
	0.91	Pt - blackened
	0.238	
Tungsten	0.07	Clean, fresh
	0.18	Clean, long-heated
	0.19	Gas-filmed, fresh
	0.55	Gas-filmed, long-heated
	0.057	Clean, fresh; 22°C.
	0.046	Clean, fresh; -78°C.
	0.025	Clean, fresh; -194°C.
	0.17	Clean (old)
	0.82	Gas-filmed, old
Nickel	0.048	Gas-free; 90°K.
	0.077	369°K.
	0.413	Gas present 90°K.
	0.343	369°K.

In general, the filament of a Pirani will have a film of adsorbed gas atoms (or molecules) since Roberts[49] has shown that to free a wire from such adsorbed layers, it is necessary to 'flash' it at a comparatively high temperature by passing a high current through it. This was never done with the gauges as we used them. The value adopted for tungsten is that found by Roberts for a fresh, gas-filmed surface; for platinum, Knudsen's value[51] is considered reliable by Kennard; for nickel, the values reported by Raines[52] in the presence of gas are roughly averaged. These figures together with accepted values for the temperature coefficient of resistance, and total emissivities for the solid elements are collected in Table 20. The radiation constant in the Miller equation will, of course, include the emissivity of the element. From the factor $a\alpha/\sigma$, in this table, it is clear that nickel is not necessarily the best element to use as filament material, though it has certain practical advantages. An interesting possibility emerges from the values for copper. No accommodation coefficient for helium (or indeed any other gas) on copper appeared in the literature, but even if one adopts a comparatively poor value of 0.2, the result factor $a\alpha/\sigma$ has a higher value than for nickel, and obviously

TABLE 20

Comparison of Filament Material*

Element	a_{He}	Temperature coefficient (x 10^4)	Total low temperature emissivity	$\frac{a\alpha}{\sigma}$
Platinum	0.44	39	0.05	0.034
Nickel	0.40	43	0.12	0.012
Tungsten	0.19	51	0.02	0.048
Copper	0.2 (say)	38	0.15	0.051

*Data (other than a_{He}) taken from "Handbook of Chemistry and Physics".

if 'a' is greater than 0.2 the factor is proportionately higher. If one were to use fine copper as filament wire some method of increasing the length of wire would have to be adopted, since the specific resistance of copper is 1.78 compared with 11.8 for nickel. Alternatively, one might employ copper wire of finer dimensions than 0.03 x 0.005 mm., though the difficulties involved in handling such wire might be very great.

It is obvious from the foregoing discussion that for equal volumes of two monatomic gases, under precisely similar conditions

$$\frac{\Delta_1}{\Delta_2} = \frac{Ka_1 / M_1^{\frac{1}{2}}}{Ka_2 / M_2^{\frac{1}{2}}} \tag{4}$$

where Δ_1 and Δ_2 are the respective galvo deflections; since

$$E = \frac{k_1' \cdot p a_1}{M_1^{\frac{1}{2}}} \quad ; \quad p = k_1'' \cdot a_1$$

$$E = k_1''' \cdot \Delta_1 a_1 / M_1^{\frac{1}{2}}$$

Equation (4) thus reduces to

$$\frac{\Delta_1}{\Delta_2} = \frac{a_1}{a_2} \cdot \sqrt{\frac{M_2}{M_1}} \tag{5}$$

For the gases helium and neon, which are of particular interest to this work, results on the relative sensitivities with the present type of Pirani gauge are easily available. As previously noted, reliable values of the accommodation coefficients are not easily found and for the case of both helium and neon on nickel under the same conditions no values were discovered in the literature. However on platinum, the value of 0.49 (helium) and 0.65 (neon) have been reported. On the basis of the theory of Lennard-Jones and Devonshire[50], the ratio of any other metal may be expected to be about the same. If this assumption is correct, one can substitute in equation (5)

$$\frac{\text{sensitivity for He}}{\text{sensitivity for Ne}} = \frac{0.49}{0.65} \cdot \sqrt{\frac{20}{4}}$$

$$= 1.7$$

The actual experimental value varies slightly from day to day, but an average value would be about 1.9, in good agreement with the above figure, especially in view of the uncertainties in the values for the accommodation coefficients.

One further result of interest can also be deduced from equation (5). Although the accommodation coefficients for hydrogen and deuterium have been reported to be slightly different[53], in general one expects two isotopic gases to have the same value of 'a'. If this is the case for helium, for a mixture of ^{3}He and ^{4}He one has

$$\frac{\text{sensitivity to } ^3\text{He}}{\text{sensitivity to } ^4\text{He}} = \sqrt{\frac{4}{3}} = 1.15$$

Hence, one should be able to deduce the composition of mixtures of the two isotopes if standard mixtures are available for calibration; this question is of interest in relation to the work on the helium content of meteorites. Although the mass ratio for the helium isotopes is 4/3, and for hydrogen, 2/1 is sufficient to give rise to different values of 'a', one should note that there is only physical interaction for a monatomic molecule for helium on a metal, whereas for hydrogen and deuterium, one has a diatomic molecules, with the further possibility of chemisorption.

PART II

STUDIES ON ISOTOPIC EXCHANGE IN HETEROGENEOUS SYSTEMS

CHAPTER V. HETEROGENEOUS ISOTOPIC EXCHANGE REACTIONS

Va. Introduction

During recent years, research on isotopic exchange reactions, in both homogeneous and heterogeneous systems, has been greatly increased. This is no doubt partially due to the wider availability of radioactive isotopes in all parts of the periodic system. The published reviews of Haissinsky[54], Edwards[55] and Amphlett[56], and the reports of three conferences on isotopic exchanges[57], show the range of this type of work.

In this thesis, the following definition will be adopted:-

> An exchange consists in the reciprocal replacement of an atom, electrically neutral or charged, radioactive or stable, in a molecular entity by another atom of the same atomic number but of different mass, arising from another (or the same) molecular entity.

One must assume, further, that the same exchange phenomena take place between atoms of the same atomic number and mass, although no technique exists for following this directly. Clearly, it is the difference in mass emphasised in the definition which allows of measurements on a given system. The two entities considered above may differ either in chemical state or constitution, or in physical state, or in both. The definition implies certain conditions essential to a precise study of any exchange reaction:-

1) The exchange must not be accompanied by any chemical change in the system leading to a decomposition of one entity, or a transfer of material from one species to the other. The exchange of the tracer atom, in a simple isotopic exchange, is due to the existence of a dynamic equilibrium between the two entities, so that the exchange occurs in conditions such that there is no free energy change in any other part of the system. Thermodynamically, the exchange

proceeds spontaneously (allowing for any energy of activation) because the approach to a uniform distribution of the tracer isotope between the two entities corresponds to an increase in the entropy of the system.

2) The rate of the process is independent of the entity marked with the tracer. In other words, if k_1 and k_2 are the rates of the reactions, $^*A \xrightarrow{k_1} B$ and $^*B \xrightarrow{k_2} A$, where the asterisk indicates the tagged species, $k_1 = k_2$. It is particularly important to verify this relationship in cases where an exchange may be confused with a chemical reaction or some surface effect.

3) The so-called "isotope effect" is neglected, so that $A^*/A = B^*/B$ at equilibrium. When an active nuclide is used as a tracer, the above relationship implies equality of specific activities of each compound or phase considered. This is not valid, in the case of light elements such as hydrogen, nitrogen and carbon. For hydrogen, mass ratios of 1:2 and 1:3 may occur; in the case of carbon-14, much work has been published on the fractionations which may occur in ordinary chemical processes[58].

4) The energies involved in the exchange must be of thermal order, which excludes hot atom reactions from the definition. The high kinetic and excitational energies of such atoms may bring about exchange reactions which do not normally occur; this type of study is closely connected with the Szilard-Chalmers effect and other chemical changes consequent upon nuclear reactions.

Within these limitations, isotopic exchange investigations have been used to obtain information on the nature and strength of chemical bonds; on individual steps in chemical reactions; on the velocities of reactions near to equilibrium; and on simple electron exchange system such as Fe^{2+}/Fe^{3+}.

Vb. Heterogeneous Systems

Although much of the published work on isotopic exchange phenomena is concerned with exchanges in homogeneous systems, the importance of heterogeneous exchange reactions has not been disregarded. As early as 1915, Hevesy[59] showed that the exchange in the system $Pb/Pb(NO_3)_2$ was rapid enough to involve several hundred atomic layers of the metal in one minute. Many authors have sought correlations between the rate of exchange metal/ion and the electrochemical properties of the system. Other data which may be deduced from such experiments relate to the processes taking place at metal/solution interfaces. This question will be discussed later.

In a comprehensive series of experiments on the exchanges between Pb, Bi, Au, Cu, Sb, Mn, Te, La, Co and Ta, and their ions, Haissinksy and his co-workers[60] have investigated the effect of time, concentration, pH, temperature and the state of the surface on the kinetics of the processes concerned. For most of the metals investigated, the exchange involved of the order of hundreds of atomic layers of metal during a few minutes contact with solutions approximately 0.1 M. The variation of the exchange with time over one or two hours followed the empirical relation $x = bt^a$, where x is the percentage exchange in time t; a and b are constants which vary from one system to another. The effect of the anion and of pH are both considerable; the exchange is favoured by conditions causing chemical attack on, or modification of, the metal surface. No relationship could be found between the rate of exchange and the electrochemical potential of the system. Changes of temperature, for experiments of short duration, lead to values for the activation energies of the processes. These values depended on the anion present in the solution being between 3 and 6 Kcal. $mole^{-1}$ for chlorides and between 7 and 8 Kcal. $mole^{-1}$ for nitrates.

From these results, it was suggested that a metal surface in contact with a solution of its ions may undergo reorganisation of its structure, rendering it more easily penetrable to the exchanging entity. Alternatively, a recrystallisation of the surface may take place, equally increasing the number of metal atoms coming into contact with the solution. The differences in exchange rates observed for the systems studied are thus due to the different behaviour of the metal surfaces in contact with solutions. The conclusion was further drawn that the elementary process of electron transfer $M \rightleftharpoons M^{n+}$ is itself very rapid and reversible.

Without anticipating the discussion in the next section, it is possible to identify three possible rate-controlling processes in a true exchange reaction between a metal and a solution of its ions. These possibilities are:-

1) the rate of arrival of ions at the solid/solution interface from the bulk solution phase;
2) the transfer of the exchanging atoms across the interface itself, or across the 'double layer';
3) the rate of arrival of the exchanging species at the surface of the solid from the bulk solid phase.

The first of these factors, diffusion in the solution, and also diffusion across the surface 'double layer' can generally be eliminated by vigorous stirring of the solution. If the exchange rate is governed by diffusive processes in the solid, one can in principle determine a value for the self-diffusion coefficient of the metal at the temperature of the experiment.

In the case of the exchange between certain non-metallic solids in heterogeneous systems, the exchange in a convenient time is limited to a single atomic layer; this has provided a useful method for the measurement of surface areas. The technique can also furnish information on the heterogeneity of crystal surfaces and on aging processes both in the absence of and in contact with solutions. A review by Paneth[61] gave the state of this work in 1948; the work of Kolthoff and his collaborators will be discussed later.

Vc. The Kinetics of Exchange Reactions

The kinetics of homogeneous isotopic exchange reactions have been discussed by various authors. McKay[62] was the first to show that such reactions are first order with respect to the active species present. Let us consider the exchange between two species A and B, in dynamic equilibrium, with the initial condition that B alone is labelled

i.e. $A + {}^{*}B \rightleftharpoons {}^{*}A + B$

Let a and b be the concentrations of A and B in moles.l^{-1}

x_o = initial activity of A

x = activity of A at time t

y = $(x_o - x)$ activity of B at time t

x_∞ and $(x_o - x_\infty)$ activities of A and B at equilibrium

The specific activities of A and B at t are then x/a and ${}^{(x_o - x)}/_{b}$

At equilibrium, $\dfrac{x_\infty}{a} = \dfrac{(x_o - x_\infty)}{b}$

i.e. $x_o = x_\infty . \dfrac{a + b}{b}$

The rate of exchange can be defined by a constant R such that

$$-\frac{dx}{dt} = R.\frac{x}{a} - R.\frac{(x_0 - x)}{b} \qquad (1)$$

R may be a function of the concentrations of the constituents and of the other molecules or ions present.

e.g.

$$R = k^1 [a]^m . [b]^n . [H^+]^p . [c]^r \qquad (2)$$

On introducing into equation (1), the value of x_0, one obtains

$$\frac{dx}{dt} = \frac{R}{ab} \cdot [(a + b)\ (x_\infty - x)]$$

or

$$\frac{dx}{x_\infty - x} = \frac{R}{ab} \cdot (a + b)\ dt$$

which, on integration, gives

$$-Rt = \frac{ab}{a + b} \cdot \ln\ (1 - x/x_\infty) \qquad (3)$$

or for given values of a and b

$$-kt = \log\ (1 - x/x_\infty) \qquad (4)$$

Clearly, a graph of the log of the unexchanged fraction (i.e. $1 - x/x_\infty$) against time should yield a straight line passing through the origin. From equations (3) and (4) one can state the conditions of the time of half-change

$$\text{i.e.}\quad t_{\frac{1}{2}} = \frac{ab}{(a + b).R} \cdot \ln 2 = \frac{0.693}{k} \qquad (5)$$

As in all kinetic studies, in order to establish the mechanism of the reaction, one must examine the variation of the rate of exchange with concentration, acidity, inert salt concentration etc. Treatments of more complicated cases such as those of exchanging molecules of the type AB and AB_n, and of separation induced exchange, are to be found in the literature[63].

The quantities in the ratio x/x_∞, appearing in equations (3) and (4), can be expressed in one of several units, such as moles exchanged, activity per gram, percentage exchanged, etc. The most convenient method of writing x is as the fraction of the specific activities

i.e. $$x_t = \frac{a_2}{a_1 + a_2} \cdot 100 \qquad (6)$$

The equilibrium state (x_∞) thus corresponds to a percentage exchange of 50%.

For heterogeneous isotopic exchange systems, a first order law is still followed provided that the slowest step is the exchange itself and not any diffusive process. Thus for a solid/solution or liquid/liquid system, the rate constant is inversely proportional to the area of the surface q

i.e. $$- kqt = \ln \left(1 - x/x_\infty\right) \qquad (7)$$

The three possible rate-controlling processes for a solid/solution system have been discussed briefly in the previous section. We shall concern ourselves here with systems in which the slowest step is the arrival of the exchanging species at the surface of a solid by self-diffusion. This type of heterogeneous exchange reaction presents a method of measuring self-diffusion coefficients at temperatures compatible with the existence of solutions. Data on diffusive processes at such temperatures are normally obtained by gross extrapolation from results at much higher temperatures. The mathematical relationships between the rate of exchange and the diffusion coefficient in question have been discussed by Wagner[64], Zimens[65] and Berthier[66]. Following a procedure previously used for the kinetics of the progressive oxidation of a metal[67], Wagner has shown that the solution of Fick's law of diffusion is simplified if the exchanging species in the liquid phase is in great excess over the amount of the same species in the solid. It has been shown that under these conditions one obtains an equation of the type

$$\ln \left(1 - {}^{x}/x_{\infty}\right) = -kt + \text{const.} \tag{8}$$

analogous to (4). The value of k depends on the form and dimensions of the solid; for example, for a sphere of radius r,

$$k = \frac{\pi D}{r^2} \tag{9}$$

where D is the relevant coefficient of self-diffusion.

If the exchanging atoms in the liquid phase are not in such an excess, the exact solution of the diffusion equation

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial t^2} \tag{10}$$

is much more difficult. Berthier has presented a complicated mathematical treatment of this type of experiment. It is assumed that transfer across the surface is not opposed by any energy barrier. Activity on both sides of the surface separation is then identical. It is then shown that the rate of the transfer and hence of the exchange depends in the first place on the geometrical form of the solid and secondly on the ratio (c) of the total number of exchanging atoms in solid and liquid phases. The relationships are then solved for differing geometrical forms. Finally, one deduces relationships between ρ and τ , where

$$\rho = 1 - \frac{x}{x}$$

and $$\tau = \frac{Dt}{r^2}$$

Such relationships are quite complicated; for example, for a sphere

$$\rho = 2(3+\gamma) \sum_{i=1}^{\infty} \frac{\exp.\left(-\alpha_i^2 \tau\right)}{\gamma(\gamma+3) + \alpha_i^2}$$

(γ is a function of the geometrical form of the solid, α_i the roots of an equation used in deducing the limits of γ). Berthier presents tables from which τ can be read off for known values of ρ and c. The value for D then follows immediately; this technique has been used in the work described in Chapter II. A later paper by Berthier[68] discusses the kinetics of heterogeneous exchange reactions in which the interfacial resistance causes phase transfer to become the slowest step. This work is discussed in Chapter VII.

CHAPTER VI. THE ISOTOPIC EXCHANGE BETWEEN SELENIUM AND POLYSELENIDE IONS

VIa. Introduction

Following the series of experiments, already mentioned[60], by Haissinsky and his co-workers on the exchanges between metals and their ions, it was decided to investigate the analogous behaviour of an amphoteric element, selenium; at the same time, experiments were carried out on the system sulphur/polysulphide ions[69]. Using amorphous (red) selenium[70], the system Se/SeO_2, HCl was examined and a dependence of rate of exchange on the acidity of the solution found. The rate was considerably reduced by substituting metallic for amorphous selenium. The investigation was then extended to the system selenium/polyselenide ions in alkaline solution. To summarise briefly, it was shown that the rate of exchange was influenced by temperature, dimension of the particles of solid, equilibrium concentration of the solution and the allotropic state of the solid selenium. These points will be discussed later as they arise.

The aim of the present experiments in the first place was to resolve the anomalous temperature effect found; it appeared from the previous work that the exchange proceeded more quickly at 0°C. than at 18°C. It was then planned to extend the experiments to the exchange between metallic selenium and polyselenide ions and hence deduce a value for the self-diffusion coefficient of metallic selenium. In the event, the results did not permit this, but direct experiments on the rate of self-diffusion were carried out and substantiated the conclusions drawn from the exchange experiments.

VIb. Experimental Methods

The basic experimental technique employed in this work was that used in the earlier series of experiments. Selenium was purified by the method described by Bruylants et al.;[71]; the commercially pure element was dissolved in concentrated nitric acid, with evolution of nitrous fumes. The resultant solution was taken to dryness and the solid redissolved in water, filtered and once more evaporated to give pure hydrated seleneium dioxide as a white crystalline solid. This conversion was carried out with an almost quantitative yield. Selenium dioxide was then sublimed in a pyrex tube, electrically heated at one end, in an atmosphere of dry nitrogen; the product was collected on a water-cooled 'cold finger'. In no case was an absolutely colourless product obtained from this sublimation; traces of red selenium were always present, despite all cleaning treatments applied to the apparatus. Consequently, this sublimate was dissolved in water, filtered and hydrochloric acid added to make the solution 6N. This solution was cooled in an ice-bath and reduced with a stream of sulphur dioxide, giving a precipitate of red selenium which was separated, washed several times with water and finally dried on filter paper at room temperature. This yields the product to which we shall refer as amorphous (red) selenium; the treatments used to prepare other varieties of the element will be described later in the appropriate sections.

The preparation and properties of alkaline solutions of polyselenides has been described fully by Pappas and Haissinsky[72]. Hydrogen selenide dissolves in sodium carbonate solution according to the equilibrium

$$Na_2CO_3 + H_2Se \rightleftharpoons NaHSe + NaHCO_3$$

This reaction mixture dissolves selenium with formation of polyselenides of general formula Na_2Se_x, where the value of x increases continuously with the concentration of Na_2CO_3. The mean maximum value of 3.2 is found in solutions stronger than 0.5M, indicating the presence of NaHSe, Na_2Se, Na_2Se_2, Na_2Se_3 and Na_2Se_4 species.

The apparatus used for the preparation of solutions of sodium polyselenide and for carrying out exchange experiments is shown in Figure 17. Since solutions of polyselenides are easily oxidised by atmospheric oxygen, pure nitrogen flows through the apparatus, after being scrubbed through pyrogallol solution, concentrated sulphuric acid and calcium chloride. Hydrogen selenide is formed by the action of 20% sulphuric acid on aluminium selenide; this gas is then carried through a solution of sodium carbonate in contact with selenium powder. The condenser C prevents distillation of water from B to D following the evolution of heat in the decomposition of Al_2Se_3. The bubbling of nitrogen through the mixture in D serves to ensure good mixing; this point is particularly important in exchange experiments and it was found that the use of an inlet tube and cone-shaped vessel (as shown in the diagram) achieves this most satisfactorily. The dissolution of selenium powder can be seen to proceed rapidly in the early stages, the reaction mixture becoming deep red. Undissolved H_2Se is passed through two wash-bottles containing lead acetate solution, where it is absorbed with the precipitation of PbSe; nitrogen flows away to waste.

Aluminium selenide is prepared by heating an intimate mixture of aluminium and selenium powders in an alundum crucible. This is placed inside a larger crucible containing sand and the whole placed in a furnace pre-heated

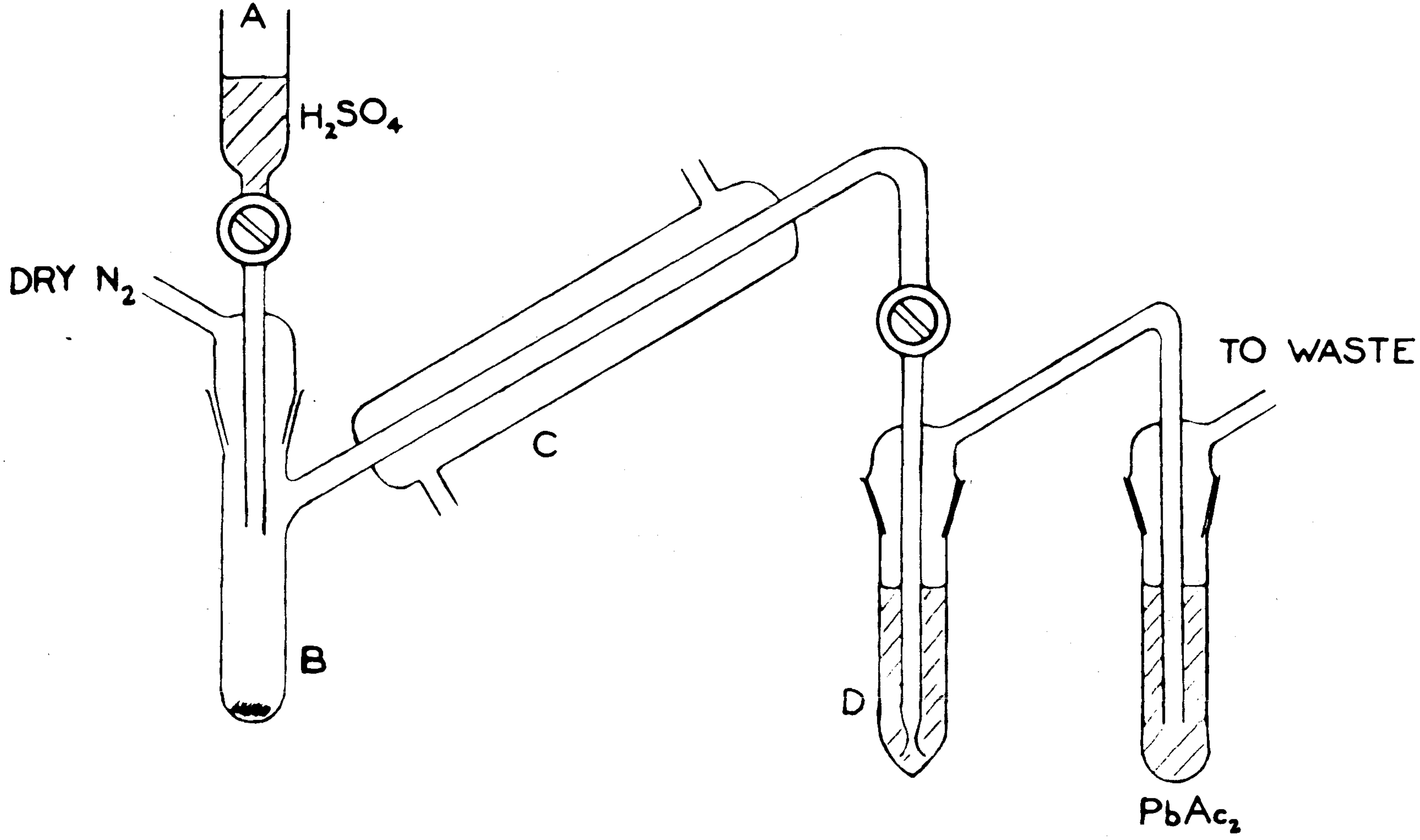


FIGURE 17

to 850°C. After about 5 minutes, a violent reaction takes place. The degree of violence depends on the Al:Se ratio, but provided this is in the region 1:9 or 1:10 as used in the present work, explosions do not occur. The product is a hard, dark-brown substance which decomposes in the atmosphere and is consequently stored over P_2O_5 after crushing in an agate mortar. The amount of Al_2Se_3 present is measured by decomposing a weighed quantity with acid in the usual apparatus (Figure 17). The amount of PbSe collected in the lead acetate solution is then collected, dried at 105°C. and weighed. Normally one found purities of the order of 70-80%.

It is worthwhile noting at this point that the decomposition of hydrogen selenide on silicone grease was not found, in contra-distinction to previous observations[72]. In fact, samples of three greases left overnight in contact with dry H_2Se showed deposits of red selenium in the increasing order Silicone $\ll$ hydrocarbon grease ('Prolabo') $\leqslant$ lubricant ('O.S.I.'). Even after three days under these conditions, the silicone grease (Dow Corning Corp., Michigan, U.S.A.) showed no deposit of selenium.

The products formed by the reaction of H_2Se on Na_2CO_3 solution in the presence of selenium powder reach equilibrium in about 3 hours. Such a solution can then be analyzed in order to check the formula of the polyselenide mixture. The solution and any undissolved selenium is poured rapidly into a 50 ml. centrifuge tube, which has been purged with oxygen-free nitrogen. The tube is closed with a screw-cap and centrifuged for about three minutes. The supernatant liquor can then be removed and oxidised with a few drops of 6% hydrogen peroxide, yielding a precipitate of selenium. This precipitate, and the undissolved selenium remaining in the centrifuge tube, are washed, collected in sintered glass filters, dried and weighed. The amount of Se obtained by oxidation of Na_2Se_x gives the total amount of combined Se; the difference between this figure and the weight of Se powder dissolved gives the amount of Se from H_2Se. One then has

$$x = \frac{\text{total Se}}{\text{total Se} - \text{dissolved Se}}$$

In all the exchange work discussed in this chapter, conditions were chosen to yield a solution containing $Na_2Se_{2.4}$, since it has been shown that in this formula region the variation of rate of exchange ($Se/Se_x^{=}$) with composition of the polyselenide mixture is at a minimum[70]. Into the vessel D is placed 20 mls. of Na_2CO_3 solution (0.12M) and about 300 mg. of Se powder; in B, one places a quantity of Al_2Se_3 equivalent to approximately 80 mg. of H_2Se. These proportions yield the appropriate solution, provided the flow of carrier nitrogen is not so high as to prevent efficient absorption of H_2Se in D. After removal of excess solid selenium from the solution by centrifuging, the solution is returned to D and 300 mg. of spiked Se powder added. These operations are carried out as quickly as possible in order to minimise the possible ingress of atmospheric oxygen. The excess selenium obtained by centrifuging is washed, dried and weighed; this weight is used as described in the previous paragraph in the establishment of the formula of the polyselenide. After a suitable interval, the solution is again centrifuged; the spiked Se powder is washed, dried and weighed in order to check that no chemical reaction has taken place, since this could result in a high apparent isotopic exchange. The polyselenide solution is oxidised and the resultant selenium collected, dried and weighed: in this way, the formula of the polyselenide is deduced.

For activity measurements the original tagged Se powder, and that resulting from the oxidation of the polyselenide solution, are counted with a bell-type Geiger counter fitted with an aluminium window. Both samples of selenium are now in the black allotropic.form, having been dried at 110°C. for some time. The samples are ground, in separate pestles, and equal weights of each counted in identical sample holders, using the method of 'infinite depth'[73]. Normally, about 100 mg. quantities were used, with a depth of approximately 5 mm. The specific activities of selenium in each phase of the heterogeneous system are then in direct proportion to the counting rates. These values are used to calculate the percentage exchange during the time of the experiment. (Section Vc. equation (6)).

Radioactive selenium (Se^{75}) was obtained from the Atomic Energy Research Establishment, Harwell. Since its specific activity was high, a small fraction was added to a much larger bulk of the inactive element; for this reason, no chemical purification of the active sample received was carried out. The active and inactive selenium samples were mixed together and then dissolved in concentrated HNO_3; this ensures completely uniform mixing of active and inactive selenium atoms. The spiked selenium is then recovered by evaporation, redissolution and precipitation by reduction with SO_2. Since the half-life of Se^{75} is long*, no decay corrections were necessary in exchange experiments; one further advantage was that the same sample of tagged selenium could be used in several experiments. For exchange experiments, finely divided selenium was ground to pass through a 300 mesh sieve. The estimation of particle size microscopically will be discussed later.

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*Several varying values can be found in the literature for the half-life of Se^{75}; this appears to be of the order of 120 days.

VIc. The Allotropic Transformation of Amorphous Selenium

As noted earlier, the isotopic exchange in the system amorphous selenium/polyselenide ions is fast, but measurable. An anomalous feature is that the rate of exchange is faster at 0°C. than at 18°. However, in the course of the reaction, amorphous selenium is transformed to the black ('metallic') allotrope.

The determination of the rate of this transformation has been carried out by placing amorphous selenium powder in contact with a freshly prepared and centrifuged solution of $Na_2Se_{2.4}$, agitated by the passage of dry nitrogen. The apparatus previously described (Figure 17) was used. Constant temperatures of 21°C. and 0°C. were maintained around the solution. At the end of a convenient (short) period, separation of the two phases was effected by pouring the mixture into a large excess ($\sim$1 l.) of oxygen-free water. The partially transformed amorphous selenium was then collected by filtration, under suction, through a coarse filter paper. The product was allowed to dry at room temperature overnight.

Analysis of the dry powder was performed by counting the number of amorphous and metallic particles under a microscope, by reflected light. Under these conditions, the contrast is sharp; particles of amorphous selenium appear bright red with no reflecting surfaces, while the metallic species has a golden hue and reflects strongly. Several hundred particles of each type were counted. The results of an experiment with contact time of $1\frac{3}{4}$ minutes are shown in Table 21.

TABLE 21

Temperature of Experiment	21°C.	0°C.
No. of amorphous Se particles	342	290
No. of metallic Se particles	62	39
% metallic Se	15.3	11.9

A further count in which agglomerates of particles, presumably resulting from the method of drying, were not counted resulted in results of 11.1% and 9.5%. The agreement in the ratios (78% and 85%) is reasonable for this method. A second experiment run for 3 minutes showed such strong visual differences that there was no doubt that the higher temperature gives the faster rate of allotropic transformation.

The rate of exchange between black selenium and polyselenide ions has been shown to be a much slower process than for the amorphous allotrope[70]. Consequently, from the above results, the effect of lowering the experimental temperature in the system amorphous Se/Se_x^{--} is to retard the formation of the slower-exchanging form, with an apparent increase in isotopic exchange. Experiments described in the next section showed that the exchange black Se/Se_x^{--} is strongly accelerated by a surface recrystallisation process. Since the allotropic transformation implies a re-arrangement of the lattice structure, it is suggested that the rapid exchanges observed with amorphous selenium are the result of an analogous mechanism. This is supported by earlier results on the influence of the formula of the polyselenide ion on the rate of exchange; following the theory of de Boer[74] on the structure of red selenium. The recrystallisation of red selenium to the black form has been noted by Ives and Pittman[75] in the course of work on the photochemical oxidation of hydrogen selenide, and also during the exchange between selenium and selenium dioxide in hydrochloric acid solution[70].

VId. Isotopic Exchange between Black Selenium and Polyselenide Ions

A sample of spiked metallic selenium was prepared by heating the amorphous variety at 110°C. for 60 hours. Using the experimental technique described previously, the relationship between time of contact (t) and percentage exchange (x) was investigated. The kinetics of heterogeneous exchange reactions have been discussed earlier; theory shows that for a reaction in a solid/liquid system, controlled by self-diffusion in the solid phase, a plot of t against log x should be linear after the rapid surface reaction is complete. In fact, no well-defined relationship was found and it further become clear that the percentage exchange for a given experimental period was not reproducible. (See Table 22 for results). It was not possible to influence the rate of exchange by irradiating the reaction mixture with a high-intensity light source, using a water filter to remove heat rays; this was considered as a possible variant by analogy with the wellknown photo-electric properties of selenium. Another factor investigated was the formation of a layer of adsorbed oxygen of varying, and possibly increasing, thickness on the surface of the metallic power, leading to the formation of a film of selenium (by oxidation of polyselenide) on immersion in the solution. To counteract this possibility, the selenium powder used in experiment 9 was shaken for about an hour in an atmosphere of nitrogen immediately before the exchange experiment. No significant change in rate of exchange was observed. It became evident, in fact, that the age of the selenium powder was of considerable importance in determining the rate of exchange, as is illustrated in the table of results.

TABLE 22

Exchange in the system metallic Se/$Na_2Se_{2.4}$ at 21°C.

Experiment	Time (hours)	Percentage Exchange	Age of Se* (days)
1	2.55	25.6	8
2	4.23	33.5	11
3	3.58	12.9	13
4	5.55	25.8	19
5	4.08	22.6	20
6	1.22	8.89	22
7	4.67	14.4	27
8	2.50	17.0	50
9	2.55	16.5	55
10	24.50	23.5	73

Moreover, the percentage exchanges are too high for a reaction whose rate is governed by self-diffusion in the solid phase. Taking a mean value for experiments 3 to 9, one can calculate a value for the self-diffusion coefficient by the procedure of Berthier[66], from which $D_{294} = 2.5 \times 10^{-13}$ cm.^{2} sec.$^{-1}$. This result is at least several orders higher than the coefficients of self-diffusion of metals some 200° below their melting-points (for Se the melting point is 217°C.); it is 10^{10} times higher than the value extrapolated for sulphur at the same temperature[69,76]. Two experiments were carried out in which exchange at 0°C. was measured.

TABLE 23

Exchange in the system metallic $Se^{*}/Na_2Se_{2.4}$ at 0°C.

Experiment	Time (hours)	Percentage Exchange	Age of Se (days)
1	2.17	7.88	78
2	3.17	9.07	84

From these results one finds $D_{273} \approx 10^{-13}$ cm.^{2} sec.$^{-1}$, so that ΔH for the rate determining process is approximately 8 Kcal. mole^{-1}.

In order to calculate these values of D, a figure of 1μ was used as a mean radius of the particles of selenium. This was determined by measuring the diameter of several hundred particles microscopically and expressing the results as a frequency curve (Figure 18A). This technique is open to certain systematic errors, but for the present experiments the mean radius so obtained is sufficiently accurate.

The significance of the age of the selenium in determining the rate of exchange suggested some type of surface re-arrangement. Through the kindess of Prof. Trillat (Laboratoire du C.N.R.S., Belle Vue, S.-et-O.), the surface condition of the selenium powder was examined before and after experiment 10 (Table 22). Electron diffraction photographs showed clearly that despite the long annealing at 110° and at room temperature, the selenium used had a surface structure which was more crystalline after the exchange experiment. After melting a sample of selenium in vacuo, followed by slow cooling, diffraction photographs showed good crystalline structure.

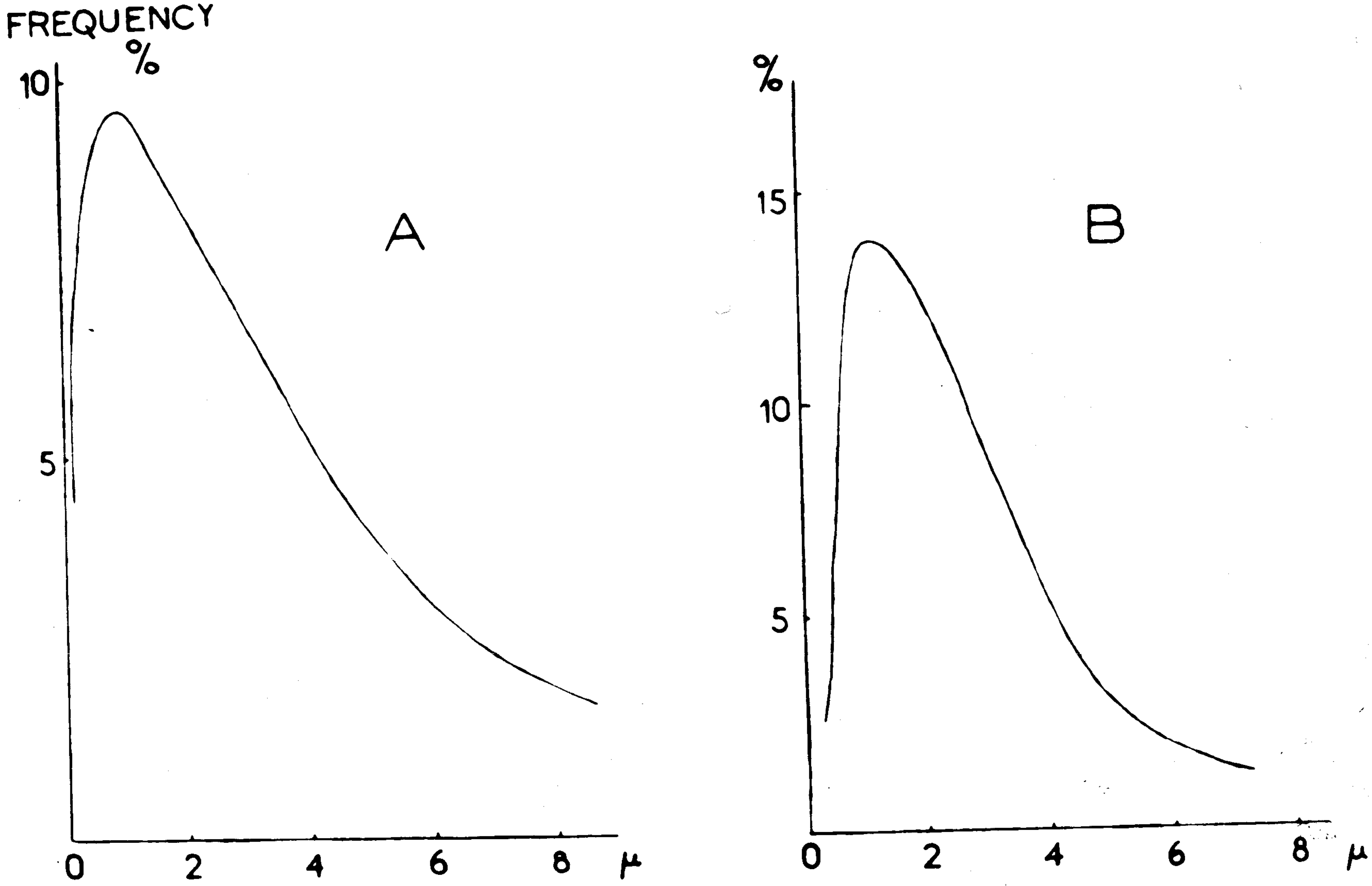

FIGURE 18

VIe. Further Exchange Experiments and Discussion

The results of experiments described in the preceding section lead to the conclusion that, in contact with polyselenide ions, black selenium undergoes a recrystallisation process by way of local dissolution and reprecipitation, consequent upon the arrival of a polyselenide ion at the end of a selenium chain in the solid. The effect of the age of the selenium upon the rate of (apparent) exchange shows that a process of perfection of the crystal lattice also takes place in the dry state at room temperature. It is not possible to analyse the results completely, since the exact mechanism and kinetics of recrystallisation processes, either in the absence or presence of a liquid phase, are not well established. However, the general trend of the exchange experiments is that to be expected if the number of surface imperfections in the solid phase is falling off with the age of the solid according to some exponential law.

It is clear from this discussion that the heating of amorphous selenium at 110°C., even for comparatively long periods, is not a method for the unambiguous preparation of metallic selenium, despite statements in the literature to this effect. The resultant solid is not completely crystalline in structure and may be regarded as intermediate in form between the amorphous (red) and metallic (black) allotropes. de Boer[74] has pointed out that differences exist between crystals of selenium grown from the gaseous phase and the 'crystalline' mass obtained by heating amorphous selenium. Examination of certain samples of selenium by X-ray powder techniques has shown that the form obtained by slow oxidation of a solution of sodium polyselenide is highly crystalline[77]. Further exchange experiments were therefore carried out with two samples of labelled selenium.

A. Fusion of a sample of selenium in vacuo was followed by slow cooling to room temperature. The solid was ground to pass through a 300 mesh sieve.

B. A solution of sodium polyselenide was placed in a loosely closed vessel and allowed to oxidise over a period of some weeks. The product was washed, dried and ground to pass a 300 mesh sieve.

The rates of exchange found with these samples are significantly lower than those quoted previously.

TABLE 24

Preparation	Time of Exchange Experiment (hours)	Percentage Exchange
A	5.10	16.6
B	6.25	3.5

It is nevertheless probable that even these values are too high for a process governed purely by self-diffusion in the solid phase, and that phenomena of surface alteration and recrystallisation are still occurring. In order to apply the method of heterogeneous exchange to the determination of the coefficient of self-diffusion, it would be necessary to use films of selenium. In this way by suitable control of dimensions, it would be possible to ensure that surface effects were negligible in comparison with volume diffusion. However, the rates of exchange in such systems, at temperatures at which aqueous solutions could be used, would necessitate the use of prohibitively long experimental times. For this reason the method was not pursued further; certain direct measurements on the self-diffusion coefficient were made and will be described in the next section.

In connection with the aging of crystals both in the dry state and in contact with solutions of their ions, it is interesting to compare the present results with those of previous workers. A general review of this subject has been given by Paneth[61]. Kolthoff and his collaborators[78] have shown that silver bromide undergoes significant thermal aging in the dry state even at room temperature. For lead sulphate[79], thermal aging at temperatures below 400°C. was attributed to movement of lattice ions to points of lower energy on the surface of the crystal; the age appeared to reach eventually a final state characteristic of the annealing temperature employed. Following Kolthoff, recrystallisation in the presence of a solution by the type of agglomeration known as Ostwald ripening is only a secondary effect. In the present work as shown in Figure 18B, no significant increase in the size of the selenium particles was detected after long contact (Table 22, experiment 10). One notes also that the energy of activation deduced for the $Se^{*}_{black}/Na_2Se_{2.4}$ exchange is of the same order (8 Kcal. $mole^{-1}$) as that found in other exchange experiments[60] in which surface alteration and recrystallisation have been shown to influence the rate of exchange.

It seems appropriate to emphasise here that the determination of self-diffusion coefficients from heterogeneous exchange experiments may lead to results which are not confirmed by direct measurements, even in cases where the kinetic data are apparently in agreement with theory. In the next chapter, the system Hg/Hg_2^{++} will be discussed. For sulphur, results from exchange data[69] differ considerably from those from more conventional experiments[76] both in rate of diffusion and in variation with temperature. Similarly, values from the Ag/Ag^{+} exchange[80] differ markedly from those extrapolated from direct measurements at higher temperatures[81]. (It is understood that the authors of this work have since agreed that self-diffusion in the solid phase is not the rate-controlling process in this exchange[82]). There is no doubt that much valuable information is to be obtained from heterogeneous exchange experiments, but it may well be that the determination of self-diffusion coefficients is one of the less useful of the applications of the method.

VIf. Self-Diffusion in Metallic Selenium - Introduction

Studies of self-diffusion in solids, liquids and gases have become increasingly prolific in recent years; the results have been applied to an understanding of transport phenomena and of liquid and solid structure. Self-diffusion implies a diffusion of something into its exact counterpart; since such a process cannot be followed, one actually measures the interdiffusion of an active or (less frequently) inactive isotope of mass almost identical with that of the bulk material. It has been shown, for example, that for the self-diffusion of Na^{22} and Na^{24} ions in solution, the isotope effect is negligible[83].

The basic law governing diffusive processes is that first stated by Fick:-

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where D is the diffusion coefficient, C the concentration of the diffusing species, x the co-ordinate along which diffusion proceeds and t the time. This equation can be integrated in various ways, but three forms have been widely used, governing the following experimental boundary conditions.

(i) A uniformly infinitely thin layer of tracer is allowed to diffuse into an infinitely thick diffusion medium.

(ii) A uniform infinitely thick layer of tracer is allowed to diffuse into an infinitely thick diffusion medium.

(iii) A uniform layer of tracer of finite thickness is allowed to diffuse into an infinitely thick diffusion medium.

The dependance of the diffusion coefficient on the absolute temperature T is given by

$$D \quad = \quad A.\ \exp.\ (- {}^{E}/RT) \qquad (2)$$

in which E is the activation energy, A a constant and R the gas constant.

Diffusion rates in solids are low and since there are generally limits to the time of the experiment, only the most sensitive methods can be used. These are generally one of the following two types.

(iv) Measurement of change of tracer concentration versus diffusion time at constant coordinate, generally the surface.

(v) Measurement of change of tracer concentration versus coordinate along the direction of diffusion for a given time.

Conditions (i) and (iv) have been combined in experiments in which diffusion of an α- or β- active nuclide has been followed by measuring the change in surface activity. This method depends effectively on the absorption of the emitted particle, or the recoiling nucleus, by a successively increasing thickness of the bulk medium. This technique has been used to measure the self-diffusion coefficients of lead[84], bismuth[85] and copper[86]. More recently, a similar approach, apparently simple and rapid, has been described by Russian workers[87]. This type of experiment suggested itself for the selenium work since the long-lived isomer of Se^{79}, which occurs as a fission product, emits a low-energy β-particle allowing sensitive measurements.

Unfortunately, the fission-yield is low and it was not possible to obtain useful quantities of this nuclide commercially.

The use of procedure (v) under the boundary conditions of (i) has been described in several publications. The solution of Fick's law under these conditions gives the equation

$$C = \frac{C_o}{\sqrt{\pi Dt}} \exp. (-x^2/4Dt) \qquad (3)$$

for diffusion in one direction. C_o represents the product of the thickness of the tracer layer and the concentration of tracer at t = o and x = o; C is the concentration of tracer at t and x. The determination of the concentration gradient by measuring the activities of successive thin sections which can be removed by milling, dissolving or grinding from the surface. Since equation (3) can be written

$$\log C = x^2 (- {}^{0.1086}/_{Dt}) + \text{constant} \qquad (4)$$

a plot of log C against x^2 should result in a straight line, from whose slope D is simply derived.

VIf. Self-Diffusion in Metallic Selenium : Experimental

In following the technique described above, rods of metallic selenium were prepared by vacuum fusion of pure selenium powder, followed by slow cooling and annealing. The end-faces of these rods were ground flat and highly polished; rods of 3 mm. diameter and 6 mm. length were generally employed. There are several difficulties in forming the necessary thin layer of active selenium on the polished face. Electrolysis has been widely used in similar experiments, but for selenium this is not feasible at low concentrations (necessary to yield layers of high specific activity) and furthermore does not readily yield uniformly thin layers of metallic selenium[88]. In the method finally evolved, a thin film of molten selenium, of high specific activity, mounted upon a flat-ended glass rod, was barely brought into contact with the polished face of the selenium rod; this caused a thin layer to adhere strongly to the latter. Polishing this active layer in a suitable holder gave a uniform layer, approximately 10^{-3} cm. thick.

Diffusion anneals were carried out in close-fitting pyrex tubes, contained in evacuated outer tubes, at temperatures controlled to within ± 2°C. Since no lathe or microtone was immediately available, analysis after diffusion was performed by removing successive layers on sections of fine emery paper, so that thin layers of uniform dimensions were available for counting. A similar technique has been developed independently by Drickamer[89]. The thickness of these layers was found both by measuring the change in length and change in weight of the rod. after the removal of each fraction. Before this sectioning procedure, the cylindrical surfaces of the rod were removed completely in order to eliminate any effects due to surface diffusion.

VIg. Self-Diffusion in Metallic Selenium : Results and Discussion

For experiments carried out below 170°C., complex diffusion profiles were obtained and these experiments were rejected. Fisher[90], and Hofmann and Turnbull[81], have shown that for pure volume diffusion or pure grain-boundary diffusion, graphs of $\ln C$ against x^2 should be linear (following equation (4)); for mixed volume and grain-boundary diffusion, a linear graph of $\ln C$ against x should result. It was later shown that the method of preparation of selenium rods used in the present experiments yielded polycrystalline material. This was demonstrated by X-ray examination carried out by Dr. R. Phillips (Department of Geology, University of Durham) who showed the selenium to be in the form of randomly orientated crystals, less than 10^{-2} mm. in diameter. Dr. Phillips' co-operation is gratefully acknowledged. With two experiments carried out at 195°C. and at 175°C. it was possible to differentiate between D_V and D_B (the coefficients for volume and grain-boundary self-diffusion). For the run at 195°C., the results are shown in Figure 19. A plot of log C against x is linear (Figure 19A) and the curve of log C versus x^2 can be analysed into two straight lines; the deepest penetration is due to grain-boundary diffusion. From this one finds

$$D^{V}_{195} = 1.6 \times 10^{-11} \text{ cm.}^2 \text{ sec.}^{-1}$$

Analogous results at 175° yield

$$D^{V}_{175} = 8.5 \times 10^{-12} \text{ cm.}^2 \text{ sec.}^{-1}$$

from which one deduces

$$D^{V} = 2.75 \times 10^{-7} \exp. \left(- 13,300/_{RT} \right) \text{ cm.}^2 \text{ sec.}^{-1} \qquad (5)$$

At 105°C. however, log C varies in a linear fashion with x^2 (Figure 20), giving

$$D^{B}_{105} = 1.8 \times 10^{-11} \text{ cm.}^2 \text{ sec.}^{-1}$$

It is clear that the generalised equation for D^V is not established to a high precision, since only two results are incorporated. Furthermore, these values may well be average values in themselves, since it is probable that the rate of diffusion in the direction parallel to the orientation of the -Se-Se-Se- chains is different to that in the direction normal to these chains. Taylor[91] has suggested that movement by transfer along the chain may enhance the rate of diffusion. These problems could be investigated by the use of large single crystals; the preparation of such crystals is in itself a problem requiring considerable study. Their use should yield unequivocal results for the coefficient of volume self-diffusion.

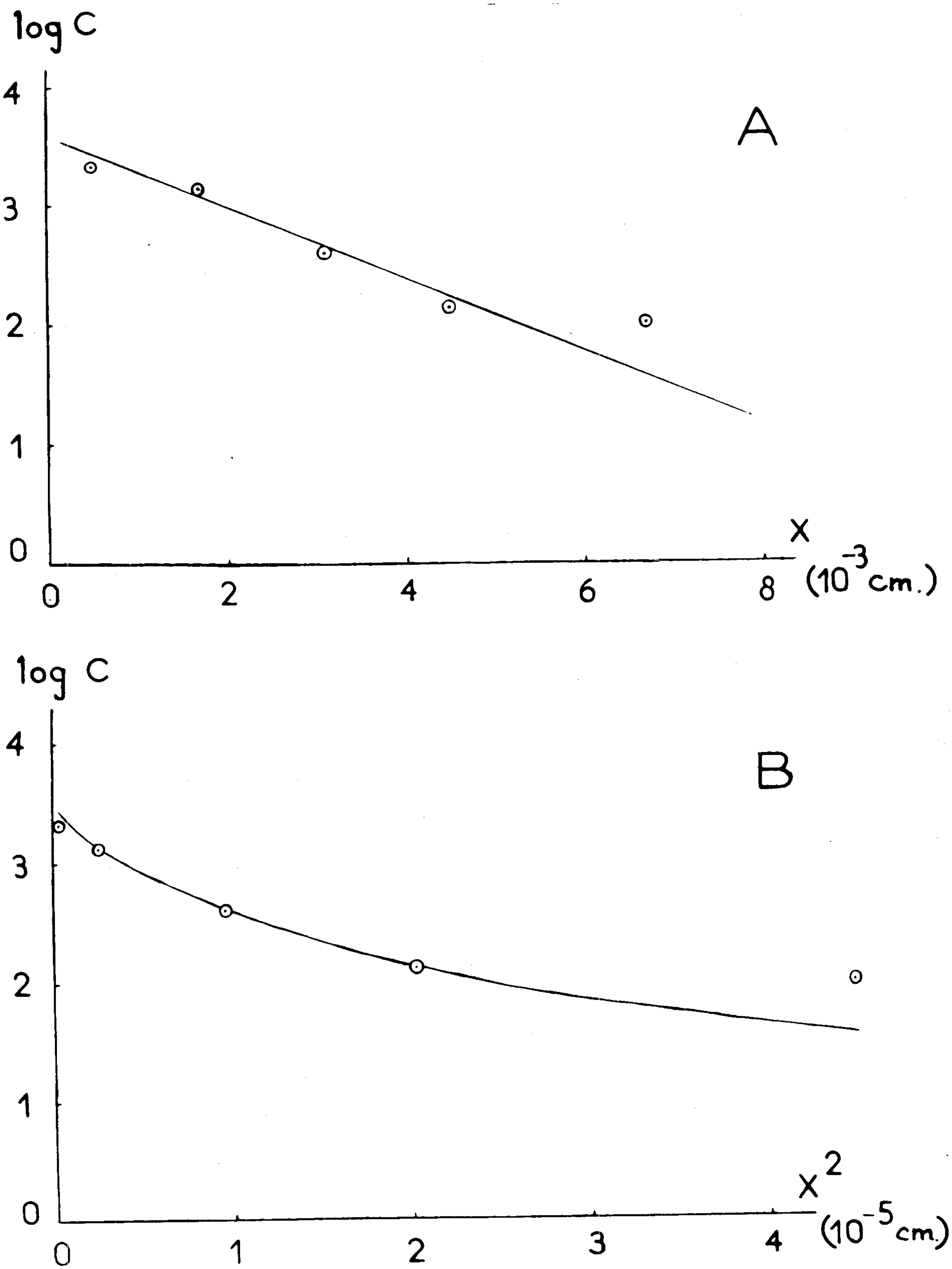

FIGURE 19

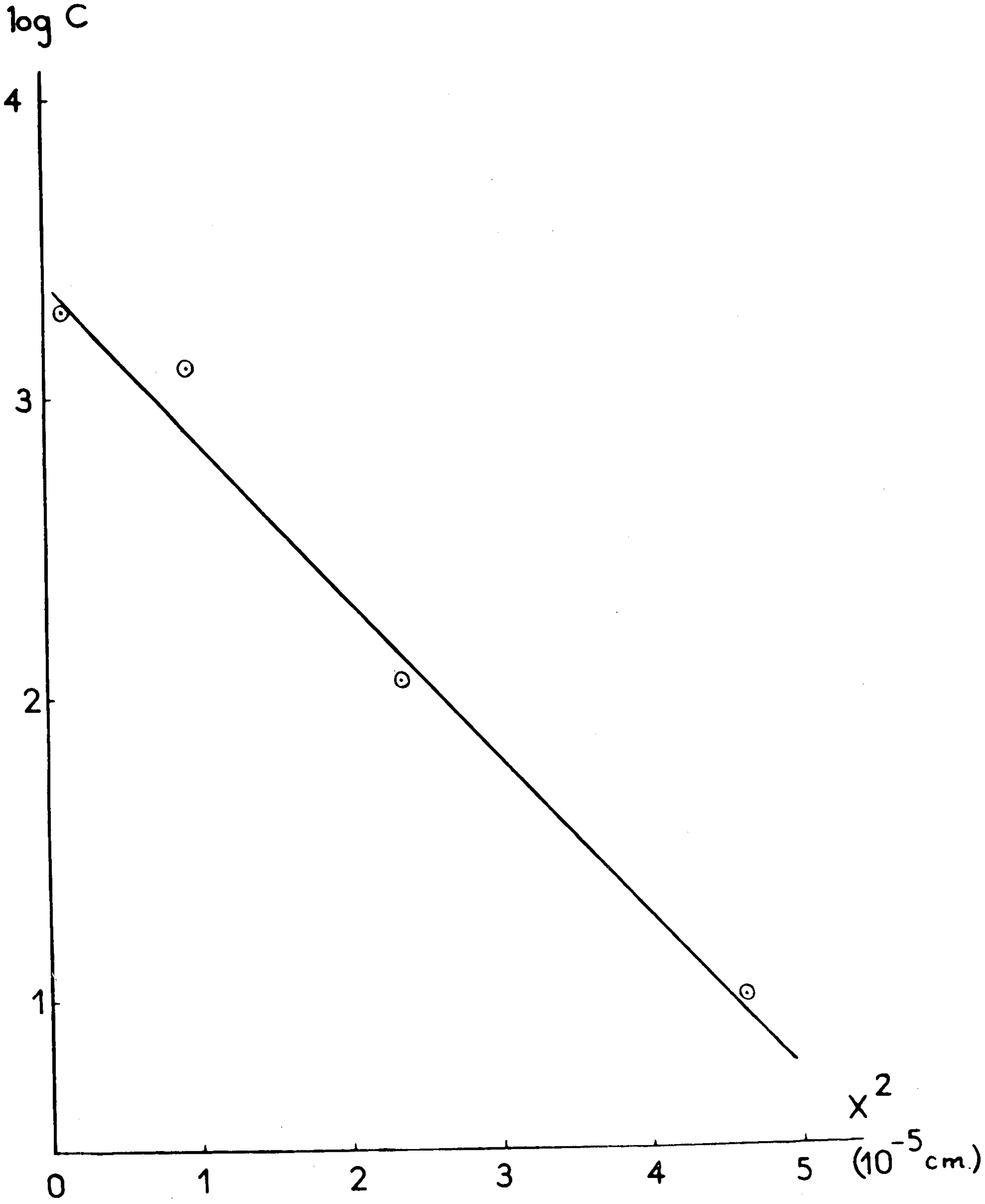

FIGURE 20

The results obtained show nevertheless that self-diffusion in the solid phase cannot have been the rate-controlling process in the exchange experiments discussed earlier. From equation (5) one calculates D_{20}^{v} as 2.80 x 10^{-15} cm.^{2} sec.$^{-1}$ which is lower than the figure given previously (Section VId) by two orders of magnitude. In view of the small particle size used in the exchange experiments, the effect of grain boundary diffusion should be quite negligible.

CHAPTER VII. THE ISOTOPIC EXCHANGE BETWEEN LIQUID MERCURY AND MERCUROUS IONS

VIIa. Introduction

From the results of the early experiments of Haissinsky and his co-workers[60], the hypothesis was presented that in metal/ion systems, modifications to the surface of the metal caused an increased rate of exchange. Exper ments on the exchange between liquid mercury and mercurous ions were then carri out[92], since such modifications are hardly possible with a liquid metal. The results confirmed this, inasmuch as the rate of exchange did not vary with the two anions used (nitrate and chlorate). In a later publication, Haissinsky and Cottin[93] investigated the mechanism of the exchange reaction by varying the geometrical form of the liquid mercury (small droplets or a cylindrical globule) and by varying the rate of stirring of the solution. The final conclusion was that the rate-determining process was self-diffusion in the liquid metal. From the experimental results, a value of approximately 5×10^{-8} cm.^{2} sec.$^{-1}$ was deduced for the coefficient of self-diffusion of mercury at 20°C. The mathematical treatment of this type of experiment presented by Wagner[64] and by Zimens[65] (see Section Vc) was used in interpretating the results. Berthier[6 in his first paper on the theoretical problems of such exchange reactions suggested that the surface resistance was in fact not infinitely small as equilibrium, but that since this effect becomes less and less important as equilibriu is approached, no significant change was necessary in the value for the self-diffusion coefficient.

A re-examination of these results became necessary in view of the direct measurements of the self-diffusion of liquid mercury by Hofmann[94]; using the capillary technique, this author found:

$$D = 1.26 \times 10^{-4} \exp. (^{-1160}/_{RT}) \text{ cm.}^{2} \text{ sec.}^{-1} \qquad (1)$$

This equation gives self-diffusion coefficients of the order of 10^{-5} cm.^{2} sec.$^{-1}$ at room temperature. Furthermore, the activation energy found is quite different to that reported by Haissinsky and Cottin.

Several recent publications[95-98] have been concerned with the kinetics of transfer reactions taking place at the interface of two liquids. Experimetal work has been mainly with pairs of immiscible or partially miscible solvents. The exchange reaction between mercury and mercurous ions is of interest in this respect not only because of the gross physical differences between the two liquid phases, but also because in this type of experiment, the system is virtually at equilibrium.

VIIb. Experimental Method and Results

The capillary technique first described by Anderson and Saddington[99] was used to compare the rate of diffusion of mercury into liquid mercury and into a solution of mercurous nitrate. Thick walled capillaries were used; their lengths were measured with a micrometer and the internal diameter estimated by measuring the length of a weighed thread of mercury. Both these measurements were reproducible to better than ½%; lengths of 2-3 cm. were used of tubing 0.425 cm. radius. Radioactive mercury was supplied by C.E.A., Chatillon and by A.E.R.E., Harwell as the element and diluted as necessary before use. Re-distilled mercury was used as the bulk phase; in the solution experiments, analar mercurous nitrate was employed, in approximately 0.05M solution. This solution was shown to be free from chloride ion.

The experimental arrangement is shown in Figure 21. The capillary is attached to its holder with a low-melting wax. The whole arrangement is

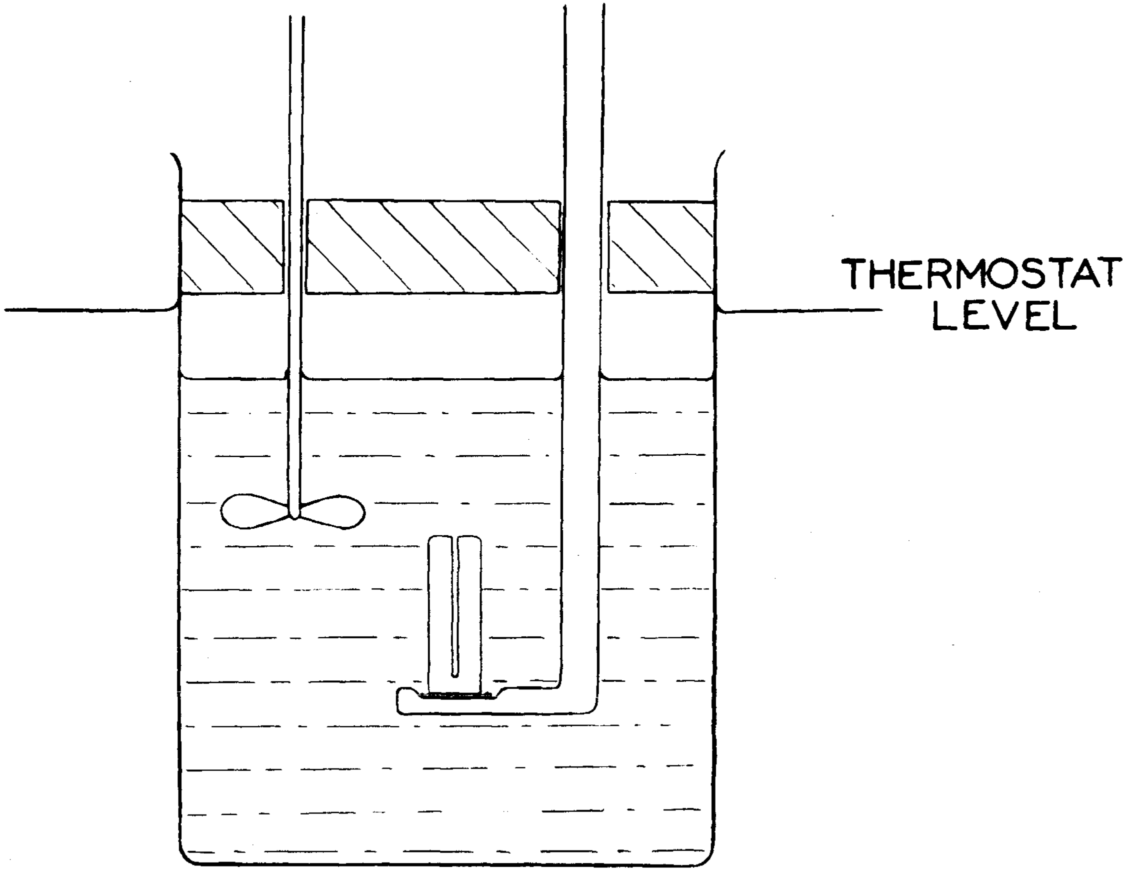

FIGURE 21

placed in a thermostat at 25°C. with the tip of the capillary projecting slightly above the surface of the liquid. After allowing a few hours for the system to come to equilibrium with the thermostat, the capillary is immersed completely in the bulk phase. This experimental set-up allowed the capillary and its holder to be removed from the solution. The capillary could then be easily washed and detached. The activity of the mercury could then be counted directly without removing it from the capillary. For this, the open end was sealed with the minimum amount of cellulose tape and placed in a standard position some 25 cm. from an end-window type Geiger tube; this method minimises geometrical errors and at the same time eliminates those involved in dissolution, source preparation etc. An identical capillary was used as a standard source of active mercury and allowed corrections to be made for the decay of the isotope Hg^{197} (isomeric half-lives 25 hours and 64 hours) during the time of the experiment.

In both series of experiments the bulk liquid phases were stirred at about 200 r.p.m.; the blades were about 5 cm. from, and level with, the mouth of the capillary. No significant difference in the rate of exchange was detected when the mercurous nitrate solution was unstirred (Table 25). The importance of the position of the stirrer and the rate of stirring has been discussed by Kennedy[100]. It seems probable that certain effects obtained by Cottin were due to violent agitation causing eddy diffusion in the liquid mercury, which would enhance the rate of exchange.

It has been shown elsewhere[99] that in the integration of Fick's law of diffusion under the conditions of the capillary type of experiment one has

$$\gamma = \frac{8}{\pi^2}\left[e^{-\theta} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \dots \right] \qquad (2)$$

where γ is the fraction of the original amount of the radioactive isotope which is left in the capillary cell at the end of a diffusion experiment of time t; and $\Theta = \pi^2 Dt/4l^2$ where D is the diffusion coefficient and l is the length of the capillary tube. This expression can be re-arranged for high values of γ and t,

$$D = \frac{4l^2}{\pi^2 t} \left(\ln \frac{8}{\pi^2} - \ln \gamma\right)$$

$$= \frac{9.21 l^2}{\pi^2 t} \left(\log \frac{8}{\pi^2} - \log \gamma\right) \qquad (3)$$

The results of two experiments on the self-diffusion of liquid mercury are given below:

TABLE 24

	Time (Hours)	γ	D (cm.^{2} sec.$^{-1}$ x 10^5)
1.1	63	0.158	1.85
1.2	49.3	0.191	2.02

The average of these results is

$$D_{25} = 1.93 \pm 0.08 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$$

From Hoffman's equation, one calculates D_{25} to be 1.77 x 10^{-5} cm.^{2} sec.$^{-1}$. In view of this agreement, these experiments were not pursued further.

For measurements on the mercury/mercurous ion system, a slightly different procedure was adopted. The rate of exchange is so slow across the small interfacial area that even after 63 hours, for example, γ is only 0.949. The activity of the capillary cell was therefore counted as quickly as possible and the cell then returned to the mercurous nitrate solution. In this way it was possible to get at least two results on a single capillary. Graphical extrapolation of a graph of -log γ against t was then used to give an average value of γ which was then inserted in formula (3) above. The results of this procedure are given in the following table:

TABLE 25

	Time (Hours)	$D_{apparent}$ ($cm.^2$ $sec.^{-1}$)
2.1	63	6.5×10^{-8}
2.2	49.3	
2.3	38.3	
3.1	24.5	5.5×10^{-8}
3.2	64.7	
3.3	45.8	
4.1	49	2.5×10^{-8}

The following points should be noted of these results. The first group is in good agreement with the self-diffusion coefficient of Cottin; this point is discussed later. In the second group of experiments the effect of dissolved oxygen on the system was investigated. Oxygen was dispelled from the mercurous nitrate solution by prolonged boiling; during the actual experiment a current of oxygen-free nitrogen (see Section VIIb)was bubbled through the solution. The apparent self-diffusion coefficient found shows that no film of oxidised material was present on the mercury surface; such a film could have presumably caused a high resistance to transfer. The result also confirms that no oxidation-reduction reaction of the type suggested by Weiss[101] is concerned in the Hg/Hg_2^{++} exchange.

During the third experiment the solution remained unstirred. In a parallel experiment involving the diffusion of mercury (from a capillary) into unstirred mercury the self-diffusion coefficient fell to 1.48×10^{-5} cm.^{2} sec.$^{-1}$.

In an experiment to compare the effect of mercurous ion concentration, solute concentrations of 0.125 and 0.005 M were used. After approximately 100 hours, using shortened capillaries, one found

TABLE 26

	Concentration Hg_2^{++}	γ
5.1	0.005	0.847
5.2	0.005	0.876
5.3	0.125	0.835

The duplicate run on the stronger solution was unfortunately lost. In view of the 25-fold change in mercurous ion concentration these results can be taken as demonstrating the absence of any concentration dependent factor, confirming Cottin's earlier work.

In order to show that the results on the Hg/Hg_2^{++} exchange are not due to an anomalously slow diffusion of mercurous ions in solution, the self-diffusion coefficient of this ion was measured in approximately 0.1 M solution in a single experiment at 25°C. A small volume of this solution was stirred overnight in contact with a globule of active mercury. The labelled mercurous nitrate was placed in a capillary cell which was immersed in the bulk phase in the usual way. In an experiment of 23.8 hours, one finds $\gamma = 0.535$ and hence $D_{25} = 1.18 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. This value may be rather inaccurate, due to the low specific activity of the solution, but shows clearly that the self-diffusion coefficient is in the same order as other cations. Kolthoff and Miller[102] have calculated a value of 0.92×10^{-5} cm.^{2} sec.$^{-1}$ from polarographic data.

One further significant experiment was performed. A capillary containing labelled mercury was placed in a solution of mercury in water prepared by shaking liquid mercury with doubly-distilled water for 5 days. Since the amount of mercury in solution is low, a pool of mercury was left in contact with the solution to provide a reservoir of the inactive element. In this case also, only a low specific activity was available; nevertheless the apparent coefficient of self-diffusion, in a short experiment, of 44 hours, was found as (approximately) 3×10^{-8} cm.^{2} sec.$^{-1}$.

VIIc. Discussion

From the work of Hofmann, it is clear that there is some process in the mercury/mercurous ion exchange reaction not revealed by the earlier work on this system. It is believed that the present experiments confirm the earlier results of Cottin, and lead to a satisfactory explanation of the kinetics of the exchange.

From the constancy of the apparent self-diffusion coefficients found in Cottin's experiments and in the present work, it is clear that the rate of interfacial transfer per unit area is constant. This is in agreement with the equation given by Davies[95] for diffusion across the interface between two liquids:

$$\frac{1}{A}\cdot\frac{dn}{dt} = k_1 c_1 - k_2 c_2 \qquad (5)$$

A is the interfacial area, $^{dn}/dt$ the rate of interfacial transfer, k_1 and k_2 the forward and reverse permeability constants, c_1 and c_2 the concentrations of the diffusing species in the two phases. For isotopic exchange reactions, $k_1 = k_2$. A precisely analogous equation can be derived from Berthier's earlier paper (ref. 66, p.529, equation 10).

In a more recent publication Berthier[68] has examined the kinetics of heterogeneous exchange reactions in which there is a resistance at the interface. This resistance changes the form of the exchange versus time graphs and gives an apparent diffusion coefficient which is smaller than the real value. It is shown that the calculated interfacial resistance in the Hg/Hg_2^{++} system is in good agreement with that found by comparing the real and apparent self-diffusion coefficients of mercury. Furthermore, it is established that the reaction constants and the energy of activation (3.1 Kcal. mole.$^{-1}$) in this system apply to a single interfacial resistance and not to a mixture of two or more processes.

Now in any solution containing mercurous ions, the following dismutation is set up

$$Hg_{2(aq)}^{++} \rightleftharpoons Hg_{(aq)}^{++} + Hg_{(aq)} \qquad (6)$$

where the species indicated are the aquated ions or atoms. The existence of an aquated mercury atom in solutions of mercury in water has been demonstrated spectroscopically by Reichardt and Bonhoeffer[103]. The rate at which this equilibrium is established has been discussed by Wolfgang and Dodson[104]. Following their argument one considers the cycle

$$\begin{tikzcd}
Hg_{2(aq)}^{++} \arrow[r] \arrow[d, "(1)"] & Hg_{(aq)}^{++} + Hg_{(aq)} \\
Hg_{(aq)}^{++} + Hg_{(liq.)} \arrow[r, "(2)"] & Hg_{(aq)}^{++} + Hg_{(g)} \arrow[u, "(3)"]
\end{tikzcd}$$

For reaction (1) at 25°C., $\Delta H_1 = 820$ cal. mole.$^{-1}$; for reaction (2), $\Delta H_2 = 14.6$ Kcal. mole.$^{-1}$ (the latent heat of vaporization). It is then assumed that ΔH_3 is similar to that for the inert gases[105] Xe or Rn, as the solubility of mercury in water is of the same order as for these elements, giving $\Delta H_3 = -4.8$ Kcal. mole.$^{-1}$. This yields an overall ΔH for the cycle of 10.6 Kcal. mole.$^{-1}$.

It follows that the dissociation energy for the above process is also 10.6 Kcal. mole.$^{-1}$ and it is assumed that for ions in solution as for gaseous molecules[106], this is approximately equal to the activation energy. If, further, the entropy of activation is small or zero[107], we can deduce from the absolute rate equation[108]

$$k = e\frac{kT}{h} \cdot \exp.(-E_{exp}/RT) \quad \exp.(\Delta S^{\ddagger}/R)$$

$$= 1.9 \times 10^{-7} \text{ min.}^{-1}$$

This argument has been invoked by Wolfgang and Dodson to explain the extremely rapid homogeneous exchange reaction in aqueous solution between mercurous and mercuric ions. This exchange is complete in less than 2 seconds for concentrations of 5×10^{-4} molar at 0°C., to be compared with half-times of approximately 50 minutes at 31.8°C. for the thallous-thallic exchange[109] at this concentration and 44 seconds for ferrous-ferric[110] at 23°C.

If the value of 10.6 Kcal. mole.$^{-1}$ deduced above is accepted, then it is clear that there can be no rate controlling process in the Hg/Hg_2^{++} exchange dependent on the rate of this dismutation. In the presence of liquid mercury, however, it has been shown electrochemically[111] that for the reaction

$$Hg_{2(aq)}^{++} \rightleftharpoons Hg_{(aq)}^{++} + Hg_{(l)} \qquad (7)$$

the activation energy is only 820 cal. mole.$^{-1}$; the equilibrium constant at 20°C. is 84.8 ± 2 (for the reverse reaction). We shall assume in what follows that reaction (7) is established rapidly in the interfacial region of the system in question.

This eliminates any other possible reaction in the solution phase as influencing the rate of exchange. For example, the dimerisation of the mercurous ion

$$Hg_{2(aq)}^{++} \rightleftharpoons 2Hg^{+} \qquad (8)$$

was considered on the grounds that the exchange Hg_1/Hg^+ might be energetically much more favourable than Hg_1/Hg_2^{++}. Since the concentration of Hg^+ ions is extremely low[112] ($k = 10^{-7}$), this could then explain the slow rate of exchange. This dimerisation however must be masked by the effects of reaction (7). Furthermore, as Gurney[113] has pointed out, to detach a positively charged ion from the surface of a metal requires a greater amount of work than to detach a neutral atom, so that a direct exchange of Hg^+ ions at the interface must be ruled out.

It is postulated then that the rate-controlling process is the physical transfer of a mercury atom from the mercury phase to aqueous phase, and that the activation energy of 3.1 Kcal.mole.$^{-1}$ is that necessary for this transfer. The possibility of a slow formation of a shell of water molecules around the mercury atom in solution can be eliminated, since Reichardt and Bonhoeffer[103] showed that only a loose coordination sphere of H_2O molecules exists around the dissolved metal atoms. Furthermore, Taube[114] has shown that for a diverse range of ions (H^+, Al^{3+}, Fe^{3+}, Ga^{3+}, Th^{4+}, Co^{2+}, Co^{3+}, Cr^{2+}, Zn^{6+}, No_3^-, ClO_4^-)

the rate of exchange between water of hydration and bulk solvent water is extremely fast. He calculates that for Fe^{2+}, the time for half-exchange of this water is about 10^{-4} min. at $0^{o}C$. This evidences indicates that even for strongly charged anions and cations, hydration shells are so loosely bound that they have practically no separate identity from the bulk phase. There can then be no reason to believe that any solvation process concerned with the formation of tightly bound hydration shells could influence the kinetics of the phase transfer reaction.

A consideration of the geometrical factors involved in the proposed phase transfer mechanism confirms the probability of this as a rate controlling step. Wang[115] has shown that in the self-diffusion of liquid water, vacancy creation is not the rate-controlling step and that the energy (4.6 Kcal. $mole.^{-1}$ at $25^{o}C$.) is that required for hydrogen bond breaking in the H_2O semi-crystalline structure. In fact, there are already sufficient vacancies in liquid water for diffusion to occur readily. Now the radius of the water molecule appears to be rather uncertain; Hofmann[94] has discussed this point, as has Wang, and suggests values between 1.5Å and 2.9Å. This latter figure is that deduced as the average nearest neighbour distance and the size of a vacancy must approximate to this. For mercury, the atomic radius is 1.5Å . These data suggest two conclusions:

(i) There should be no large energy barrier to the insertion of a mercury atom into the water lattice.

(ii) To remove a mercury atom from the liquid metal phase and move it into a vacancy in the water lattice requires a greater translational movement than is needed for self-diffusion in liquid mercury itself. This is supported by the greater activation energy required.

If, in fact the diffusing entity in liquid metals is the ion, as has been suggested for liquid mercury and liquid lead, the difference of 2.0 Kcal. required to translate a mercury atom into the solution phase is easily comprehended.

From the inference that the phase transfer is a diffusion process, we can proceed to compare its rate with the normal rate of self-diffusion in liquid mercury. The rate law for diffusion given by Eyring[116] is

$$D = \lambda^2 \cdot \frac{kT}{h} \quad \exp.(-\Delta H^{\ddagger}/RT) \quad \exp.(\Delta S^{\ddagger}/R) \qquad (9)$$

where λ is the distance between successive equilibrium positions; the other symbols have their usual significance. In comparing phase transfer and bulk diffusion, the subscripts T and B will be used. Values of D_T and D_B are already available, so that

$$\frac{D_T}{D_B} = \frac{\lambda_T^2 \cdot \frac{kT}{h} \cdot \exp.(-\Delta H_T^{\ddagger}/RT) \quad \exp.(\Delta S_T^{\ddagger}/R)}{\lambda_B^2 \cdot \frac{kT}{h} \cdot \exp.(-\Delta H_B^{\ddagger}/RT) \quad \exp.(\Delta S_B^{\ddagger}/R)}$$

$$= \frac{6.5 \times 10^{-8}}{1.77 \times 10^{-5}} = 3.67 \times 10^{-3} \qquad (10)$$

We shall put $\lambda_B = 1.5\mathring{A}$ after Hofmann, and assume that λ_T is 2.9A°, the average nearest neighbour distance for water. There is considerable uncertainty in these figures, but since they are the only non-exponential terms on the right-hand side of the equation, this is relatively unimportant. Expression (10) then reduces to

$$3.67 \times 10^{-3} = 3.74 \cdot 3.54 \times 10^{-2} \cdot \frac{\exp.(\Delta S_T^{\ddagger}/R)}{\exp.(\Delta S_B^{\ddagger}/R)}$$

$$\text{i.e. } \exp.(\Delta S_T^{\ddagger}/R) = 2.78 \times 10^{-2} \ \exp.(\Delta S_B^{\ddagger}/R) \qquad (11)$$

Nachtrieb[117] has recently given an expression for calculating $\Delta S^{\ddagger}$ for self-diffusion in liquid metals:

$$D_o = \frac{1}{6} . \lambda^2 \nu \quad \exp.(\Delta S^{\ddagger}/R) \qquad (12)$$

ν is the characteristic lattice vibration frequency which can be calculated from the formula[118]

$$\nu = 2.8 \times 10^{12} \sqrt{\frac{T_m}{MV^{2/3}}} \qquad (13)$$

Where T_m is the melting point in °K, M is the molecular weight and V the molecular volume. This formula is strictly only applicable to crystalline solids, but Nachtrieb considers it justified for liquid metals near the melting point. Equation (13) then gives

$$\nu = 2.8 \times 10^{12} \sqrt{\frac{234}{200.6 \quad 6.03}}$$

$$= 1.22 \times 10^{12}$$

so that equation (12) becomes

$$1.26 \times 10^{-4} = \frac{1}{6} . (1.5 \times 10^{-8})^2 \quad 1.22 \times 10^{12} \quad \exp.(\Delta S_B^{\ddagger}/R)$$

$$\text{i.e. } \exp. (\Delta S_B^{\ddagger}/R) = 2.76$$

This gives a value of 0.42 eu. for the entropy of activation of liquid mercury. For sodium, Nachtrieb finds a value of 0.7 eu. We can now deduce a value for ΔS_T, since

$$\exp.(\Delta S_T^{\ddagger}/R) = 2.78 \times 10^{-2} \times 2.76$$

$$\text{i.e. } \Delta S_T^{\ddagger} = -5.1 \text{ eu.}$$

It is interesting to note that Davies[95] finds a much larger negative entropy of activation in the diffusion of potassium iodide from nitrobenzene to water.

It was noted earlier that the present experiments gave values for the apparent self-diffusion coefficient in good agreement with the results of

Cottin. The mathematics treatment of both series of experiments is based in the first place on Fick's law of diffusion. The equations used by Cottin fail to detect an interfacial transfer process because Zimens[65] deals only with the case of a resistance arising from the Helmholtz double layer on the aqueous side of the interface. Following the discussion given previously it is suggested that Cottin finds diffusion as the rate-controlling process because diffusion <u>is</u> the rate-controlling process; Cottin's experiments did not show that the diffusion coefficient measured was for diffusion across the interface.

The only work immediately comparable to the present discussion is that of Miller and Pleskov[119] on exchange between amalgams of bismuth, zinc and lead and solutions of the salts of these elements. The rates found are much faster than those found for the mercury-mercurous system. Rate of exchange depends on the amount of metal in both mercury and solution phases. No rate-controlling process was identified. From a study of the data available in the abstract, it is suggested that the rate controlling step is diffusion of the solute atoms in the mercury phase; the exchange current, as the authors term it, clearly depends on the number of colliding atoms at the interface and hence on the concentration in both phases. We can support this argument by comparing the rates for zinc and lead.

TABLE 27

	Exchange for current 0.1M Solution	At. % in amalgam	Rate of Exchange per at. %	Diffusion coefficient in mercury cm.^{2} sec.$^{-1}$ x 10^{-5}
Zn	14.0	0.98	14.3	1.34
Pb	14.0	0.59	23.8	2.0

The diffusion coefficients are deduced from the data given by Cooper and Furman[120]; the diffusion coefficients for bismuth do not permit of extrapolation to the amalgam concentration used by Miller and Pleskov. It is further suggested that no phase transfer process operates in the case of the amalgam experiments, because, as Haissinsky[60] has pointed out earlier, metallic impurities can act by the formation of small local cells in discharging ions and hence augmenting the rate of exchange. For solid metals, this results in an extremely fast exchange, but for amalgams the diffusion in the metallic phase is sufficiently rapid to control the exchange rate.

On small point that should be mentioned is that the value for the self-diffusion coefficient of mercury is in good agreement with the theory of Frenkel[121], who suggests that the self-diffusion coefficient of a liquid is of the same order as the diffusion coefficients of solutes in that liquid. For self-diffusion and solute diffusion in liquid mercury, coefficients are of the order of 10^{-5} cm.^{2} sec.$^{-1}$ at room temperature.

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ACKNOWLEDGEMENTS

I wish to express my gratitude to Professor F. A. Paneth, F.R.S. for the privilege of working under him in the Londonderry Laboratory for Radiochemistry in the years 1949-52, and for his constant interest throughout this work. It is a pleasure to acknowledge the direction and help received from Dr. K. F. Chackett during his supervision of the work from 1949 until 1951, and to thank Mr. G. R. Martin, B. Sc., A.R.C.S., for the many valuable discussions on this and other topics.

I am indebted to the Department of Scientific and Industrial Research for a maintenance grant throughout the whole of this period; without such a grant, the work could not have been undertaken.

It is equally a pleasure to record my deep gratitude to Dr. M. Haissinsky for his direction of the work described in Part II of this thesis. I am grateful to the Centre National de la Recherche Scientifique for the award of an exchange fellowship, through the British Council, and to the late Madame Irene Joliot-Curie for her efforts in procuring for me a special grant from the Bourse Carnegie, of the Sorbonne, enabling me to extend the work on the mercury-mercurous ion problem.

D. G. Tuck.