Determination of radio-active constants by the measurement of helium evolved

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Saunders, Peter G. (1956) Determination of radio-active constants by the measurement of helium evolved. Masters thesis, Durham University.

UNIVERSITY OF DURHAM

THESIS

submitted for the degree of Master of Science

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"Determination of radio-active constants by the measurement of helium evolved."

Submitted: June, 1956

EXPERIMENTS ON THE DETERMINATION OF RADIO-ACTIVE CONSTANTS BY THE MEASUREMENT OF THE HELIUM EVOLVED.

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Chapter 1.

GENERAL INTRODUCTION.

Radium has long been the most important radioactive substance known. It is used widely in the medical profession and in other branches of study requiring a source of ionizing radiations, although with the advent of artificial radioactive isotopes radium is no longer the main source for such purposes. Most of the classical study of radioactive and nuclear phenomena involved the use of radium as a source of alpha-particles. Moreover, until 1950 the standard unit of radioactivity, the curie, was defined in terms of the quantity which is the subject of the present investigation, the alpha-activity of one gram of radium. The present definition of the curie, that quantity of any radioactive nuclide in which the number of radioactive disintegrations per second is 3.7×10^{10}, reflects the value of the specific activity of radium which was regarded in 1950 as most probable.

Definitions should be set down for the various quantities in terms of which the radioactive characteristics of a nuclear species can be expressed.

The half-life of a radioactive nuclide is the period of time required for the activity of any sample to fall to half its initial value. This period is independent of the initial activity. It is usually denoted by the symbol $t_{\frac{1}{2}}$.

The radioactive decay constant of a nuclide is the fractional decrease in the activity of a sample per unit time. It is given the symbol λ and is related to the half-life by the formula:

$$t_{\frac{1}{2}} = (\log_e 2) / \lambda$$

The specific activity of a nuclide may be defined as the number of radioactive disintegrations of that nuclide occurring per second per gram of nuclide. It receives the symbol Z and is related to the radioactive constant by the formula:

$$\lambda = Z M / N_0$$

where M is the atomic mass of the nuclide and N_0 is the Avogadro number.

The prominence of radium as a radioactive source is probably due to the fact that it has a long enough half-life (i.e. the specific activity is low enough) for it to be present in recoverable amounts in nature; yet it has a short enough half-life to provide a very intense source when pure. This intermediate value of the half-life has been the cause of the difficulty in the determination of that quantity. It is too long (1590 years approx.) for direct determination by following the decay of the activity, yet not long enough for accurate values to be obtained by the relative abundance in minerals. The intensity of the radiation and the nature of the daughter products makes difficult a determination of the rate of emission of alpha-particles. It is therefore not surprising that the values determined experimentally for this most important constant have varied considerably.

A large number of methods have been employed for this determination, none of which is free from objections of various sorts. Many values have been given for the specific activity, yet these values disagree with one another by amounts considerably larger than the degrees of accuracy claimed by the workers. Many of the more recent values lie near the figure 3.7×10^{10} alpha particles per sec. per gm. although few lie above this value. This was the figure adopted as the International Standard for the curie in 1950, (Ref. 1.1) but the work of Kohman and his co-workers, indicating a lower value of 3.61×10^{10} re-opened the question. At that time the accurate technique developed by Glueckauf and Paneth and others for the micro-analysis of helium offered the possibility of using with greater accuracy an old approach, the measurement of helium derived in a given time from the alpha-particles, and of that application the present study forms a part. It had been hoped that it would form the final part and that a new and important determination of the half-life would be possible. This was not achieved in the time available, yet it is hoped that this preliminary study of the problem will advance it materially towards a solution.

CHAPTER 11

CRITICAL DISCUSSION OF OTHER METHODS USED.

The methods which have been used to determine the half-life of radium are extremely numerous and varied. Only a few have been selected for discussion here but they include the most interesting and important.

Measurements of the activity of radium may be designed to determine the radioactive decay constant directly or the specific activity directly. Either having been determined, the other, and the half-life (which is intimately related to the radioactive decay constant), can be calculated. The experimental methods may be divided into two classes depending on whether the radioactive decay constant or the specific activity is the constant directly determined. A table of those determinations which will be discussed is given below, sub-divided on the basis of method:

TABLE 1

SOME OF THE MORE IMPORTANT DETERMINATIONS OF THE SPECIFIC ACTIVITY.

Class 1: Determinations of Radioactive decay Constant

Method		Worker	Date	Result
(a) Measuring decay of radium; not done in practice				units 10^{10} α/sec /gm
(b) Build-up of radium	(i)	Boltwood		
	(ii)	Gleditsch		3.47
	(iii)	Meyer & Lawson	1928	3.4
(c) Equilibrium in radium series		Wertenstein	1928	3.61

Class 11: Determination of Specific Activity

Method		Worker	Date	Result
Direct:				
(a) Visual counting of scintillations	(i)	Rutherford & Geiger	1908	3.4
	(ii)	Geiger & Werner	1924	3.61
(b) Counting of electrical pulses	(i)	Rutherford & Geiger	1908	3.4
	(ii)	Lawson & Hess	1918	3.72 3.7
	(iii)	Ward, Cave & Wynne-Williams	1929	3.66
	(iv)	Kohman, Ames & Sedlett	1951	3.61
Indirect:				
(a) Transfer of charge	(i)	Rutherford		-
	(ii)	Braddick & Cave	1928	3.67
(b) Ionization Produced	(i)	Zeigert	1928	3.71
(c) Heating effect	(i)	Hess	1912	3.75
	(ii)	Watson & Henderson	1928	3.69
	(iii)	Mann	1954	3.56
(d) Helium produced	(i)	Dewar	1910	3.7
	(ii)	Boltwood & Rutherford	1911	3.3
	(iii)	Gunther	1939	3.67

(α) Glass 1 Determinations of Radioactive decay Constant.

These methods depend on measuring the growth and decay of activity, or the equilibrium conditions in samples of radium. The possible approaches are three-fold. The decay of a sample of radium may be measured at intervals, the growth of radium in its parent substance (which is controlled among other things by the radioactive decay constant of radium) may be followed, or the equilibrium of radium with its parent and daughter substances, which gives the ratio of the half-lives, may be studied.

(a) The first approach has not been adopted in practice for the reason that the radioactive decay constant of radium is too low, being approximately 4.5×10^{-4} year^{-1}. Even over a period of 10 years the activity would only fall by 0.5%. If it were possible to provide a comparison standard that would remain constant in activity for so long, the measurement would still be of a very small change in a large quantity with a consequent hundred-fold decrease in accuracy.

(b) Build-up of Radium in Ionium.

(i) Boltwood (Ref.2.1)
(ii) Gleditsch (Refs. 2.2.,2.3.,2.4)

The second approach has been adopted. The rate of growth of radium in its parent substance, ionium, has been measured by Boltwood and also in several different experiments by Gleditsch and her co-workers. The growth of radium in ionium initially freed from radium follows an exponential recovery curve which is complementary to the decay curve and tends asymptotically to the equilibrium value as the decay curve tends to zero. The rate of growth and the rate of decay are governed by the same constant. It is a necessary condition that the curve should not be distorted by the decay of the parent substance, i.e. that the half-life of ionium should be large compared to the half-life of radium. This is so; the half-life of ionium is approximately 90,000 years. It is not necessary to know the half-life of ionium with great accuracy, nor the amount of ionium present. The two quantities which must be measured are the activity of radium in equilibrium with a given sample of ionium and the rate of growth of radium activity in the same sample after all the radium has been removed. It is not necessary to know the masses of radium involved, but the activities must be strictly comparable, all the absorption factors must be constant. The rate of growth of activity divided by the equilibrium activity is then the same as the proportional rate of decrease of activity in a sample of radium, which gives the radioactive constant.

This method is of interest and importance because it differs fundamentally from most others. It has the advantage of avoiding absolute determinations of the activity of samples. All activity determinations are comparative only. Nor does the mass of radium involved have to be measured.

In the various pieces of work referred to in this section different minerals containing ionium were used. The experiments differ in this respect chiefly and the method used is basically the same. The assumption was made that the composition of these minerals had remained constant over a period of several half-lives of radium so that equilibrium had been established. A determination of the activity due to radium in a weighed portion of the mineral gave the equilibrium value. Then from another weighed portion all the ionium was separated free from radium. The growth of radium in a solution of this ionium was followed by drawing off the evolved radon.

The best of the whole series of experiments gave a value for the radioactive decay constant of 4.11×10^{-4} years^{-1} which corresponds to a specific activity of 3.47×10^{-10} alpha particles per sec. per gm. and a half life of 1686 years. (This value of the specific activity was recalculated by Kohman using a more recent value of the Avogadro number). The value for the specific activity was lower than that of most of the recent determinations by 5 or 10%.

The two most likely sources of error are:

(1) alterations in the composition of the mineral within the last few thousand years changing the equilibrium of ionium and radium. The most likely alteration would be preferential leaching of radium, which would make the apparent equilibrium activity lower than it should be and the apparent specific activity too large.

2. incomplete separation of ionium from the mineral. If ionium were lost in the process of freeing it from the accumulated radium, the apparent rate of growth of activity would be too low and the apparent specific activity would be too low. Small quantities were used and the authors mentioned difficulties of handling. It seems likely that this error is responsible for the divergence of the result from the majority of recent values.

(iii) Meyer and Lawson (Ref. 2.5)

Meyer and Lawson also determined the rate of growth of radium in ionium. They used a sample of ionium and thorium oxides whose composition and weight was known from the atomic weight determinations of Hoenigschmidt and Horowitz. Radium had been growing in the sample for some seven years. Without opening the glass ampoule containing the sample, Meyer and Lawson determined the amount of radium present by a comparison of the gamma-ray activity due to Radium C in equilibrium with radium with that of a standard radium sample. By determining the gamma-ray activity in various directions relative to the axis of the ampoule, and estimate of the gamma absorption of the sample and its container was obtained. A value for the specific activity of 3.4×10^{10} alpha particles per sec per gm was found.

The method avoids an absolute determination of activity. However it involves a comparison of gamma activities between two samples with different geometries which is extremely difficult to do with accuracy. The gamma absorption in the walls of the containing ampoule and in the material of the sample is very sensitive to thickness and to shape and may reduce the apparent activity by several per cent. It is very difficult to estimate it with a reasonable margin of accuracy. This type of measurement is involved in several of the methods to be described and has been the subject of criticism by Kohman, Ames and Sedlett. (Ref.2.11) The uncertainty of the correction probably accounts for the poor agreement between Meyer and Lawson's value and other more recent values.

(c) Equilibrium between radium and radon.

Wertenstein (Ref.2.6)

The third method in this class involves the volumetric measurement of the quantity of radon in equilibrium with a known mass of radium. The half-life of radon is known with good accuracy and the half-life of radium can then be derived. The corresponding approach using radium and ionium is not practical because the half-life of ionium is not known as well as that of radium.

Wertenstein's method has the interest of being different from all other methods. It reduces the handling of radium to a minimum and involves no measurements of activities unless the radium source needs to be standardized. The method used for obtaining the radon is not described. Presumably it was pumped off from a standard radium source. Measures taken to ensure complete removal of radon from its parent are not described. Wertenstein found difficulty in purifying the radon from its chief contaminants, hydrogen, helium, water-vapour and carbon dioxide. Of these, carbon dioxide is similar in physical properties to radon and was difficult to separate completely from radon by physical means. The total pressure of a known volume of the two gases was measured with a Knudsen gauge and the viscosity was measured with a quartz thread.viscometer. By partially condensing carbon dioxide in a liquid air trap and repeating the measurements, the contaminating effect of the carbon dioxide could be estimated and the partial pressure of the radon found. The impact of alpha particles on the walls of the vessel caused evolution of occluded gas which was mostly hydrogen. This was burned in an excess of oxygen on a platinum wire coated with copper oxide.

Wertenstein's value for the specific activity (after correction using a recent value of the Avogadro number) was 3.61×10^{10} alpha particles per sec per gm; but the accuracy which he could claim was only sufficient to bring the margin of error down to 5%. This large margin of error which makes the experiment of doubtful value, is apparently due to the radiation driving occluded hydrogen from the walls of the vessel. Wertenstein in a foot-note reports that he freed the glass from occluded hydrogen by baking it at 450° C. but does not report any consequent improvement in accuracy. Further, one would like to know more about measures taken to ensure accuracy in the standardization of radon with regard to the radium from which it was obtained.

Class 11 Determinations of the Specific Activity.

In Class 11 are included all those methods which involve measurement of the number of alpha particles produced from a known mass of radium in a given time, and which result therefore in a value for the specific activity. The methods can be sub-divided into the 'direct' in which individual particles can be counted by some sort of recording mechanism; and the 'indirect' which depend on the measurement of some property of the alpha particles, the electric charge transferred, the heating effect, or the volume of helium produced when the alpha particles are brought to rest. The terms 'direct' and 'indirect' do not necessarily imply any great difference of approach or superiority of method, they are simply useful for classification.

(β) Class 11 Determinations of Specific Activity: Direct

(a) Counting scintillations

(i) Rutherford and Geiger (Ref.217)

The alpha particle source used in this experiment was not radium itself but a deposit of Radium B + C & C' obtained by exposing a suitable source holder to radon for a period of some hours, and allowing the active deposit that was formed to decay for about 15 min, in order that radium A might decay to negligible proportions. The source holder then contained for purposes of an alpha particle determination only radium B + C, decaying in a complex fashion which can be approximately represented by an "effective half-life" of about half an hour; and Ra C', the alpha particle emitter, in equilibrium with Radium C. The decay was followed and the source calibrated by comparing the gamma activity with a standard sample of radium. This gave a comparison of the amounts of radium C' in the standard and on the source holder. By determining the rate of alpha emission of the radium C' on the source holder at any given moment, Rutherford found the rate of alpha emission of the radium C' in the sample. But the latter was in equilibrium with a known mass of radium, so the specific activity of the radium could be determined.

The source holder was placed at a suitable distance from an aperture of known area. This distance was large compared with the dimensions of the holder and could be decreased as the source decayed.

In this series of experiments the alpha-particles passing through the aperture fell on a zinc sulphide screen and the scintillations caused were counted visually through a fifty power microscope. The result given by Rutherford and Geiger was 3.4 x 10^{10} alpha particles per sec per gm but a

5 - 10% margin of error was considered possible.

The use of a radium B + C deposit as a source has the advantages that the source is easily prepared and handled. It is extremely thin so that there is no danger of scattering as the alpha particles pass through the material of the deposit. Only one nuclear species, effectively, is being measured so that the beam of particles is quite homogeneous. Hoever the comparison with the sealed standard using gamma activities is a source of weakness as discussed above. (Sec.α(b)(ii)) The rapid decay of the source means that the gamma ray intensities must be determined simultaneously with alpha particle measurements and long periods of observation are impossible. To define a narrow beam of alpha particles by means of an aperture involves scattering at the edges of the aperture, and possibly scattering through the aperture of particles from outside the beam which had struck the walls of the experimental vessel or the source holder. Finally visual counting with a zinc sulphide screen is extremely tiring for the eyes, and scintillations may be missed through fatigue.

<u>Counting scintillations:</u>

(ii) Geiger and Werner (Ref.2.8)

These authors also used a zinc sulphide screen, giving considerable care to its preparation. They observed that there were minute grains of zinc sulphide on a prepared screen which gave a fluorescence when struck, but that only 590/600 of the grains were thus active. Geiger and Werner made a screen thin enough for scintillations to be seen on both sides but thick enough to ensure that every alpha particle striking it should pass through several grains of zinc sulphide. Thus only 0.4% of the alpha particles passed unrecorded. To eliminate the effects of eye fatigue, they placed the screen at an angle of 45° to the alpha particle beam and arranged for it to be observed from both sides simultaneously. (see Fig.1) The observers recorded electrically every scintillation they saw, and most scintillations which escaped the notice of one observer were recorded by the other.

The source used was an unusual one. (Fig. 1 b). A small conically shaped vessel A had for its base a thin window of mica B. This vessel was filled with radon and inert carrier gas to a pressure of a few cm of mercury through a platinum capillary tube C which was then sealed. The thin window was placed against the mica window D of the recording apparatus. An alpha particle emitted in the direction of the recording apparatus from anywhere in the gas space or from the active deposit on the walls would pass directly into the recording apparatus. The latter consisted of a long evacuated tube E with a small accurately measured aperture F at the end distant from the source. The tube contained two or three diaphragms H with small holes in the centre, such as would not cut off alpha particles proceeding directly through the aperture, but would prevent any particles being scattered through it from the walls of the tube. All the particles passing through the aperture fell on the screen G and were counted visually through two microscopes, I. The source was calibrated by comparison with a standard sample using gamma ray intensities in the way mentioned previously. The alpha particles of radon, radium A and radium C' were measured in some cases and, in others, all the alpha particles but those arising from radium C' were cut out by means of thin filters. The authors gave a final value of 3.4 x 10^{10} alpha particles per sec per gm (-0.8% or +2%).

The source used has the advantage over a radium B + C' source that it decays with the half-life of radon, thus avoiding the errors involved in a more rapidly decaying source. To have two observers of the screen is an improvement upon the system of Rutherford and Geiger. However the value obtained for the specific activity is lower than most of the recent values, and it is possible that the screen was less efficient than was thought, and that a significant proportion of the alpha particles were scattered out of the beam in their passage through the residual gas in the long tube. Some of the radon may have been occluded on the walls of the platinum capillary tube. Insufficient allowance may have been made for the scintillations that were missed by both observers. A correction was made for this, based on the assumption that observer A would observe his normal proportion of the scintillations missed by observer B. However B would be most likely to miss those scintillations which occurred near the edge of the field or nearly simultaneously with others. These are just those which A would be likely to miss. Therefore the number of scintillations missed altogether was probably larger than estimated. The results of experiments using radon + radium A + radium C' differed from those using radium C' only by 1.4%,a rather large margin. It is an unavoidable disadvantage of this experiment that many of the errors tend to make the result too low, as is indicated in the figures for the probable margin of error given by the authors.

(b) Counting pulses of ionization.

(i) Rutherford and Geiger. (Ref. 217)

This experiment is parallel to that carried out by the same authors and already described under the heading 'counting scintillations' . The source used was the same as that already described. The counting instrument was a rudimentary form of proportional counter. A wire connected to a Dolezalek electrometer ran down the middle of a tube, the casing of which was maintained at a high negative potential. The inside of the tube contained gas at a low pressure. Alpha particles were allowed to enter through an aperture of known area. The primary ionization caused by the alpha particles was multiplied by collision in the high electric field and was collected on the centre wire. The resulting electric pulses caused ballistic throws of the electrometer. These throws were recorded by an observer. This simple arrangement was capable of recording only three or four particles per minute with accuracy. Long periods of counting were therefore required which was difficult with the rapidly decaying source used. The advantage of this apparatus over the zinc sulphide screen lay in the fact that readings were possible over several hours, whereas an observer can only watch a fluorescent screen for two or three minutes without tiring.

The result obtained by this method (3.4×10^{10} alpha particles per sec per gm) agreed with the scintillation counting experiment of the same workers within the limits of error.

(ii) Lawson and Hess. (Ref.2.9)

This determination was regarded for some time as one of the best. The source used was a deposit of radium C and Ra C' on a hemispherical holder. It was calibrated by a comparison of gamma ray intensities with one of the secondary international standards kept at Vienna. The source was placed at the end of an evacuated tube 4 m long and was moved closer to the measuring instrument as the intensity of the source decayed. This was done in order to keep the counting rate approximately constant.

The measuring instrument was a development of Rutherford and Geiger's "pulse ionization" counter. A hemispherical piece of thick copper sheet was kept at a high negative potential. Alpha particles entered through a small aperture of accurately known dimensions and struck a collecting electrode placed in such a position as to receive them all. The showers of electrons produced when the alpha particles passed through the gas at a moderately low pressure within the hemisphere, were multiplied by the accelerating voltage and also struck the electrode. The counter, when filled with air at 40 mm pressure, counted a proportion of beta and gamma rays as well as alpha particles; but pure carbon dioxide or mixtures of 54% or more carbon dioxide and air at the same pressure allowed only alpha particles to be counted, because in these mixtures the primary ionization of the alpha particles was not multiplied sufficiently to trigger the counter. The counting rate was between 30 and 50 per minute and the background counting rate was 6 per minute, which set a limit to the accuracy of the exper experiment. The pulses actuated a unifilar electrometer which gave a ballistic throw to a spot of light on a glass scale. At first the throws were observed visually but there was a marked discrepancy between the reports of the two observers. A value of $(3.72 \pm 0.02) \times 10^{10}$ alpha particles / sec / gm was given for the specific activity. In a later experiment the movements of the spot of light were recorded photographically.

The resolving time of this instrument was 1/5 sec approximately but this was uncertain. Since the correction factor involved for coincident pulses at the counting rate used is 0.92, this uncertainty clearly affects the accuracy of the experiment. A plot of observed activities against counting rate was given by Lawson and Hess. When produced back to zero counting rate it gave a value of 3.7×10^{10} alpha particles per sec per gm. As the authors admit, the accuracy of the experiment does not warrant saying more than that the value lies above 3.6 and near 3.7×10^{10} alpha particles per sec per gm.

The advantages of the method lie in the fact that only alpha particles are counted, which was not the case in earlier counters of this type. Also it eliminates the subjective element in visual observation by using photographic recording. In other respects it suffers from the general disadvantages of a gamma-ray standardization, a rapidly decaying source, and a small aperture, that have been mentioned and from the particular disadvantages of a high background count and a long resolving time.

(iii) Ward, Wynne-Williams and Cave (Ref.210)

The source used in this experiment was similar to that of Rutherford and Geiger in that it used a Radium+ B'+ C + C' deposit and similar to that of Geiger and Werner in the precautions taken to secure an accurately measured beam.

The radium B + C + C' source was prepared by exposure of a source holder to radon and calibrated by means of its gamma activity, a decay curve being drawn. The source holder (A in Fig.2) was placed in an evacuated vessel V containing an aperture B of known area, covered with a mica window C. The source was covered with a brass cap D, containing a mica window E, to cut off all recoiling nuclei. There was also a shutter F which could cut off the direct beam and enable the background to be determined with the source in position. This enabled correction to be made for the ionization produced by the gamma radiation of the source, which of course passed only slightly diminished through the shutter.

The mica window over the aperture separated the source holder section from the measuring instrument section which was not evacuated but contained gas at a pressure of some cm of mercury. The alpha particles were detected by means of the ionization they produced. However the ionization was not multipled in the gas space (as in the two methods just described). The primary ionization only was collected on a wire passing down the centre of the instrument. The applied electric field was sufficient to collect the ionization quickly but not sufficient to accelerate it to the point where it might cause collisional ionization. The pulse produced by this ionization was then amplified by a valve amplifier to give a pulse capable of actuating head-phones or an electric pen. Pulses separated by 1/100 of a second were resolved and there was an estimated statistical error of 0.2%. Beta particles, which produce much less ionization, gave practically no pulse and a useful check on the homogeneity of the alpha particle beam was given by the amplitude of the pulses. Two particles entering the counter simultaneously gave a pulse of double amplitude. Only radium C' alpha particles and a small proportion of radium C alpha particles were being used in this experiment and particles with significantly lower energies (producing smaller pulses) must therefore have been scattered from some solid object. The background counting rate of this instrument was very low.

Estimates were made of the effect of scattering. In the collodion slip, stopping power 1 mm, covering the source the number of particles scattered out of the beam would be about the same as the number scattered in, and in any case would be very small. The pressure of gas in the space between the source and the aperture was varied without having an effect on the counting rate greater than the normal statistical variation; so scattering of particles by the gas must have been negligible. It was considered possible that the effective size of the aperture to alpha particles might have exceeded the measured geometrical aperture by an amount not more than 0.3% of the total area.

The value obtained for the specific activity was $3.66 \times 10^{10} \pm 0.5\%$ alpha particles per sec per gm.

The advantages of this type of counter lie in its counting efficiency, which is greater than that of the Geiger type counter. With the latter there may not be sufficient amplification in the gas space to record a pulse. In this apparatus the only function of the collecting electrode is to collect the primary ionization, which may be done with an efficiency of nearly 100%.

One disadvantage is the indeterminacy in estimating the scattering of alpha particles. This occurs in all methods where the sample is mounted on a support and the beam of alpha particles limited by means of an aperture. Secondly, the comparison with a standard by means of gamma ray intensities has already been criticized. But on the whole, this work commands respect as one of the most careful and reliable of determinations.

Counting Pulses of Ionization

(iv) Kohman, Ames and Sedlett (Ref. 2.11)

We now pass to one of the most recent experiments, which has already been mentioned in the general introduction. The source used by these workers was radium itself, directly weighed. This was done to avoid the errors of a comparison by means of gamma activities, which the authors regarded as a grave source of error. Samples weighing 3 mg and others weighing 50 µg were used. Results from each individual sample agreed closely, but results from different samples showed a scatter somewhat greater than the statistically probable error. The authors regarded the weighing therefore as their biggest source of error. The samples of $RaCl_2$ were dissolved and portions containing from 0.1 to 0.5 micrograms were pipetted on to flat platinum discs and evaporated carefully to dryness. They were examined under a microscope and those which showed that the deposit of any thickness extended to the edge of the disc were rejected. The deposits should have weighed less than 1 microgram but in fact they appeared to contain several micrograms of material which may have been platinum from the attack on the discs of the intense radiation and the dilute acid in which the samples were dissolved. The deposit was not smooth but arranged in ridges of up to 20 microns thick and in some places up to 50 microns thick. The range of radium alpha particles in most solids is 25 microns, and the authors found no evidence of appreciable self-absorption; and low-angle scattering does not matter here.

As soon as the discs had been examined they were inserted into a parallel plate alpha counter which recorded all the alpha particles leaving the upper surface of the sample. The efficiency of this counter was determined by standardizing with a plutonium 239 source, which had been previously determined in a counter whose counting efficiency could be accurately calculated from its geometry. The parallel plate counter had an efficiency somewhat greater than that indicated by the geometry factor. 0.515 of all the alpha particles emitted were counted. This was due to low-angle back-scattering from the sample disc and its holder.

As with all instruments that count individual pulses, the parallel plate counter suffers from having a period after each individual pulse during which the counter returns to its normal condition. Particles entering during this period will not be recorded. This period is called the resolving time or the recovery time, and although it can be reduced to a very short period indeed it can never be entirely eliminated and a correction has always to be made. In this case the correction was up to 2% and the estimated error introduced by this and other counting errors was 0.1%.

The counting continued for an eight-hour period. All the radon and much of the short-lived deposit was removed during evaporation of the radium solution. As radon built up and the short-lived deposit initially present decayed, the curve of activity versus time tended to the theoretical growth curve. In calculating these growth curves the Bate man equations had to be modified by introducing two factors to allow for (a) radon emanating from the solid, which is proportional to the concentration of radon at any given moment, and (b) for recoiling atoms of radon which escaped from the solid at a rate depending on the rate of decay of radium. Other recoiling atoms were charged and were recollected on the source plate. The loss due to diffusion of radon out of the solid was small. The curve was not sensitive to this factor during the first eight hours and a constant correction could be applied. The recoil loss factor had to be determined for each sample. This was done by drawing a series of growth curves for different values of the recoil loss factor and fitting the experimentally observed curve. Various degrees of fit were distinguished and statistical weight given to the best. A smaller apparent recoil loss was observed for those measurements which were carried out over a shorter period of time, but no reason could be found for this.

A value of $(3.608 \pm 0.028) \times 10^{10}$ alpha particles per sec per gm was given for the specific activity of radium.

The advantages of the method to which the authors call attention include the avoidance of a gamma-intensity calibration, the use of radium as a source, and the avoidance of some of the indeterminate corrections that are found in the 'indirect' methods. An additional advantage is the straightforward counting arrangement which determines all the alpha particles emitted over a whole hemispherical arc.

However there are various disadvantages apparent in the method. The large recoil loss and the fact that it is not constant make it important that the effect should be allowed for properly. The process of matching curves is not a very satisfactory one and, as the authors admit, satisfactory curves could not always be obtained. The experimental curves already differed from the theoretical because of the decay of short-lived deposit initially present. Also the subjective criterion introduced to determine whether or not a source was satisfactory gives rise to the possibility that some of the plates which were passed as satisfactory had in fact lost radium. Also the method of determining the efficiency of the parallel plate counter attracts attention. The counter was standardized by a source which had been previously determined in a counter of known efficiency. But it is extremely difficult to be certain of the efficiency of any counter. There is no way of being certain that every alpha particle is in fact recorded neither can one be certain that no scattering occurs. In fact the problem of a 100% efficient counter is a crucial one for all the methods described in Class 11. Kohman refers to Kovarik and Adams (Ref. 2.11b) who described a collimating grid for a flat source and gave a method of analysing the efficiency of this as a source. Kohman used such an arrangement for calibrating his ~~pol~~plutonium source but does not explain how the counting efficiency of the counter used with this collimating grid was determined.

Nevertheless, this experiment has some important advantages over all others and ranks as one of the most important of the determinations of the half-life of radium.

(γ) Class 11 Determinations of Specific Activity: Indirect

(a) Transfer of charge

(i) Rutherford (Ref. 2.12)

This was one of the earliest determinations of the specific activity of radium. Alpha particles from a thin flat deposit of radium were allowed to strike a parallel collecting plate and the rate of transfer of electric charge was measured. The charge on the alpha particle was assumed to be that of a singly charged hydrogen ion. A solution of radium bromide was spread evenly on a plate of aluminium or glass and evaporated to dryness in order to provide a source which was too thin to absorb any alpha particles. This procedure removed all radon and the minimum alpha activity which was reached after three hours could be regarded as due entirely to radium. The collecting plate was a copper box and the whole apparatus was evacuated. In early experiments the effect of the alpha particles was completely masked by secondary electrons. These were removed by applying a strong electric field at right angles to the path of the alpha particles which caused the electrons to return in a curved path to the plate from which they started. There was still an appreciable current flowing due to the ionization of the residual gas. This current could be reversed by applying an opposite voltage to the source plate, the alpha particle current being not appreciably affected. The source used was calibrated by comparing it with a standard radium sample using the gamma activity due to radium C.

The results obtained by Rutherford, when corrected using more recent values for the charge on the electron were so much lower than those of other workers as to render the experiment of historical interest only.

Transfer of charge:

(ii) Braddick and Cave (Ref.2.13)

The principle of the method is the same as that of the experiment just described, and the source was a radium C and Ra C' deposit, whose emitted alpha particles were passed through a small aperture in the same manner as in the work of Ward, Wynne-Williams and Cave, described in an earlier section. The source holder was much nearer the aperture in this work and an effective solid angle of aperture for the source as a whole was calculated by the method of zonal harmonics.

The measuring instrument consisted of an evacuated vessel containing a shallow copper box, facing the incoming alpha particle beam. The box was connected to a Compton electrometer which was used as a null reading instrument by balancing the growing voltage on the box with a known voltage from a potential divider. The capacity of the collecting system had been accurately measured and the rate of increase of charge on the collecting plate could thus be accurately measured. An applied magnetic field was used to deflect all beta particles and it was found that this could be done without appreciably affecting the stream of alpha particles. Braddick and Cave also found that the alpha particle current was not affected by varying the potential of the collector plate within quite wide limits. At first anomalous results were obtained due to the emission of delta ray electrons from the flat collector plate at glancing angles along the lines of the magnetic field, but after the plate was changed to a shallow box this no longer occurred. The collector was of very thin copper foil, sufficient to stop all alpha particles but too thin to collect an appreciable number of beta particles or to permit an appreciable photo electric effect caused by gamma rays.

Braddick and Cave gave a value of 3.68 x 10^{10} alpha particles per sec per gm after the first series of experiments but later changed it to 3.69 x 10^{10} ± 1% alpha particles per sec per gm. Using more recent results for the value of the charge on the electron, Kohman has corrected this latter figure to 3.67 x 10^{10} alpha particles per sec per gm.

The advantages of this method lie in the simplicity of the recording apparatus. There being no triggered pulse mechanism, there is no recovery time during which particles cannot be recorded, therefore a larger source and a larger flux of particles can be used.

The disadvantages are:

1. the assumption that all the alpha particles carry a double positive charge.

2. The effect of electrons is comparatively large. In a counter depending on scintillations or ionization or heating effects, the influence of electrons is small, but here the loss or gain of one electron at the collector has half the effect of an alpha particle. The emission of secondary electrons from the collecting plate is possible even with the precautions that were taken. Electrons arising from the gamma radiation which penetrates to all parts parts of the apparatus may strike the collecting plate or be driven from the collecting plate, hence it is important to conduct an accurate background count with the source in position and the alpha particle beam interrupted by a shutter. This was in fact done.

3. The effect of scattering alpha particles is not large with the large aperture used, but the authors give no estimate of what it might be.

4. The usual objection can be lodged against the standardization of the source by a gamma ray comparison.

This experiment gave a result in agreement with that of Ward, Wynne-Williams and Cave to within 0.3% and appears to be among the most reliable.

(b) Measurement of Total Iônization Produced.

(i) Ziegert (Ref.2.14)

A value for the specific activity of radium arises almost incidentally out of work done by H. Ziegert, and a result obtained by Fonovits-Smereker (Ref.2.15). The former measured accurately the number of ion pairs produced by a single alpha particle and used the latter's value for the ionization current produced by the radium C' in equilibrium with a known amount of radium to arrive at a value for the specific activity of radium.

In Ziegert's work a layer of radioactive material was spread on the inside surface of a metal sphere whose diameter was larger than the alpha-particle range at the gas pressure used (usually one atmosphere of carbon dioxide). A calculable proportion of the emitted alpha-particles came to rest in the gas-space within the sphere and the ionization caused in the gas during the passage of these particles was the same for all particles of a given nuclear species. This ionization was collected on a wire in the middle of the sphere under the influence of a strong electric field. The wire was connected to the needle of an instrument resembling a quadrant electrometer and each alpha particle causes a deflection of the electrometer. The capacity of the electrometer wire and its deflection under a known voltage was carefully measured, so that the deflection provided a measure of the change of electric charge on the wire in the sphere. It was shown that the apparent ionization produced by a single particle was more or less independent of the collecting field over a wide range, indicating that all the ionization was collected with a moderate field. A large number of deflections of the electrometer were analysed statistically. It was found that a large proportion of them were deflections of the same well defined magnitude corresponding to alpha particles that came to rest in the gas-space. Deflections of smaller magnitude were due to alpha- particles which struck the walls before the end of their flight. Any larger deflections would be due to alpha particles from contaminants or decay products. From the magnitude of the preferred deflection Ziegert calculated that 1.36 x 10^5 ion pairs are produced by the radium alpha particle.

We must also consider the work of Fonovits-Smereker. She used a radium C + radium C' source on a flat piece of gold foil and calibrated it by a comparison of gamma activity with a standard source. She estimated a 1.5% error in this determination due to the background radiation of the laboratory. The gold foil was placed on the lower of a pair of parallel plates which were separated by a distance greater than the range of the alpha particles. The ionization current was measured for various values of the electric field between the plates and for various values of the distance between the plates. By covering the source with a piece of leaf-tin, alpha particles could be cut out and the ionization due to beta particles and gamma rays was thus estimated as 6% of the total. Different results were obtained using different metals as holders of the Radium C source. Gold was found to be the best.

It was found that a saturation ionization current of 1.952 x 10^6 e.s.u. was produced by the Ra C in equilibrium with 1 gm of radium. Using this result with his own, and making use of an equation connecting the total ionization of any alpha particle to the 2/3 power of its range (Ref. 2.16) Ziegert derived a value for the ionization charge produced by a single radium C' alpha particle and hence found for the specific activity of radium 3.71 x 10^{10} alpha particles per gm per sec.

The advantages of the ionization current measurement are that alpha particles produce far more ionization in a small gas space than do beta or gamma rays, so that the effect of the latter is less than, say, in the measurement of charge directly carried. The measurement is more exact than that of heat produced, and there is not the 'recovery time' uncertainty that there is in pulse ionization counters.

The disadvantages of these two experiments, which must be considered together for our purposes, lie mostly in the measurement of ionization current, which is open to the criticisms, (a) that the gamma standardization of the source is only accurate to within 1½% and (b) that no correction is made for ionization due to recoiling nuclei and to alpha particles scattered at low angles from the metal supporting the source. The last effect may be considerable, as Kohman, Ames and Sedlett found. Ziegert's own measurement is limited by the accuracy (1%) with which the magnitude of the electrometer deflections can be measured, and the thickness of the source (which is not mentioned in the paper but is probably negligible). Apart from these considerations the measurement of Ziegert appears very reliable. Great weight should not be given, however, to the final value for the specific activity.

(c) Heating Effects.

(i) Hess (Ref. 2.17)

In 1912 Hess carried out a careful experiment on the heating effect of radon and its decay products. A sample of radium chloride was analysed and crystallized; it weighed 570.1 mg. It was sealed and inserted in one of two identical calorimeters in an insulated box. In the other calorimeter was a heating coil which was adjusted to keep the two calorimeters at the same temperature. The rate of heating was plotted as the daughter products of the radium grew.

After a month and a half a value for the equilibrium heating was obtained by extrapolation. Using the formula:

$$Q = Q(Ra) + Q(E)\ (1) - e^{-\lambda t})$$

where Q(Ra) is the rate of heating due to radium and Q(E) is the rate due to the daughter products (λ of course is the radioactive constant of radon) values for Q(Ra) and Q(E) were obtained. It was assumed that all the beta rays and 18% of the gamma rays were absorbed within the calorimeter.

Hess then assumed a value, 3.4×10^{10} alpha particles per sec per gm, for the specific activity of radium and derived a value of 1.59×10^{9} cm per sec for the velocity of the radium alpha particle on emission. Using current values of the disintegration energy of radium, and a value of 3.75×10^{10} alpha particles per sec per gm for the specific activity has been derived from Hess' figures, by Kohman. (Ref. 2.11).

The method of measuring the heating effect avoids all geometric factors involved in mounting a sample. All alpha particles are measured with complete efficiency, and the difficulties of recovering helium are also avoided. However, a very large radium sample is needed to provide sufficient heat to measure and a large number of assumptions have to be made concerning the heating contributions of beta particles, gamma rays and recoil nuclei.

(ii) Watson and Henderson (Ref. 218)

This work was undertaken to show whether or not there was any extra heating effect in radioactive decay apart from that due to the kinetic energy of alpha particles, recoil atoms, beta rays and the heating effect of gamma rays. The authors had previously made a comparison of the alpha activity of radium C + C' and thorium C in terms of equivalent gamma activities. Using this comparison and assuming the specific activity of radium to be 3.7×10^{10} alpha particles per sec per gm (after Lawson and Hess, (Ref.2.9)) they calculated heating rates for radon alone, Radium B, radium C and radium C' together, radium C & C' separately, thorium B and thorium C together, and thorium C only. Corrections to allow for decay and estimates of the fraction of beta and gamma rays absorbed in the apparatus were made. The velocities of the alpha particles were derived from Geiger's rule $v^3 = kR$ and from the value of 1.922×10^9 cm per sec given by Rutherford and Robinson for the velocity of the alpha particle from radium C'.

Watson and Henderson then measured the heating effect for the five cases above, using two identical insulated tubes, whose temperatures were compared with two identical platinum resistance thermometers fitted in adjacent arms of a Wheatstone Bridge network. One tube served as a control, into the other was placed a radioactive source; and the heating effect was observed. The source was then replaced by a small heating coil, the current through which was adjusted until an identical heating effect was obtained. Corrections for the time-lag of the apparatus, for conduction along the leads of the heating coil, for possible thermoelectric effects, etc. were made.

The observed results were between 98.4% and 99.2% of theoretical for the radium family, and 101.4% and 102% of theoretical for the thorium family. The thorium figures may be accounted for by the error in comparison of specific activities. The authors stated that the high degree of agreement between theoretical and observed radium figures supported Hess and Lawson's figure; 3.72×10^{10})/gm.)/ sec. but they did not derive any value of their own on the basis of the experiment. If they had done so, presumably it would have been less than that of Hess and Lawson in the ratio of observed to calculated figures giving a value of 3.68×10^{10} alpha particles per sec per gm. Using currently accepted values for alpha particle energies the value found is 3.63×10^{10} alpha particles per sec per gm. However the fact that the authors regarded a 1% discrepancy between observed and theoretical values as within the limits of experimental error show that the results do not warrant the placing of any great emphasis on the value.

The method is an improvement upon Hess' in that the various constants are more accurately known. A correction is made for the heating effect of recoiling nuclei, and the calorimetric measurements are more reliable. The principle sources of error are the uncertainty in the percentage of beta and gamma ray energy absorbed, the uncertainty in the correction for the lag of the apparatus with a rapidly decaying source, and the indeterminacy of the exact alpha particle energies.

(iii) Mann (Ref. 2.22)

Since the conclusion of this work, a series of papers has been published by Mann and his co-workers describing a new and extremely accurate determination of the rate of heat production of radium. A pair of microcalorimeters was used and the heating effect of a radioactive source in one calorimeter was balanced by the cooling effect of a Peltier junction sealed to the bottom of the source holder. The same current passed through a Peltier junction in the other calorimeter and caused a heating effect. These effects were approximately the same and the difference was measured by means of a six-junction thermocouple in each calorimeter, arranged in series in opposite senses, and in series with a galvanometer of known sensitivity. The source was then moved to the other calorimeter and the Peltier current was reversed. The galvanometer deflection was again observed. The one cup then gained 2 PC in Peltier heating (where C was the current and P the Peltier coefficient) and the other cup lost 2 PC. This difference was equal to the heating effect of the source plus or minus the difference in galvanometer readings. This method eliminated uncertainties due to Joule heating in the Peltier junction.

The Peltier junctions were calibrated by means of heating coils similar in shape and heat output to the radium sources used. These sources were the American and British National Standards prepared by Hoenigschmidt in 1934. The mass of radium element present, as originally given by Hoenigschmidt, was corrected to allow for decay of radium using a half-life value of 1620 years. (This is a small correction, and the value for the mass in 1954 is not appreciably affected by the uncertainty in the value of the half-life). An average value of 165.83 µw/mg of radium was found. From this was subtracted a correction to allow for the energy production of the polonium and radium E which would have built up, giving 151. 36 µw/mg on 30.20 cal / gm / hr for radium and daughters down to Ra D.

The gamma absorption of the source is equivalent to 0.184 cm of lead. Using results of Zlotowski (Ref. 2.23), this was corrected to an 'infinite' thickness of adsorber, giving 138.6 cal/gm/hr ± 0.5%.

To derive a value of the specific activity one can sum the energies of the emitted alpha and beta particles in the decay chain from Ra to Ra D which are all in equilibrium. The branch chain is negligible for these purposes. The beta rays and gamma rays are assumed to be all absorbed and values for the decay energies were obtained from Landolt - Börnstein (1952).

The total energy produced is

28.24 Mev /disintegration of radium

$= 1.081 \times 10^{-12}$ cals./disintegration of radium

The rate of heat production if all gamma rays are adsorbed is 138.6 cals/gr/hr.

Therefore there are 3.563×10^{10} disintegrations/sec/gm. This value is even lower than Kohman's 3.61×10^{10} and therefore lies outside the best recent results.

This is probably due to incomplete adsorption of the beta rays of Ra C in the thin-walled calorimeters, or possibly a larger correction should have been made for incomplete absorption of the gamma rays. The calorimetric method itself appears to be extremely sound.

(d) Volume of Helium Produced.

(i) Dewar (Ref. 2.19)

We come now to the method which was adopted in the work to be described in this thesis. The advantages of the helium method will be summarized separately in the next paragraph. It depends on the fact that alpha particles, being helium nuclei, produce minute quantities of gaseous helium on coming to rest. Helium is chemically inert and can be removed from the radio-active material and estimated volumetrically. The amounts produced are extremely small and a limit to the experiment is set by the accuracy with which small quantities of helium can be measured.

Dewar used a McLeod gauge, the bulb of which had been calibrated by an expansion method. The closed stem was calibrated using a thread of mercury. Quantities of solid anhydrous radium salts of the order of 100 mg were allowed to stand for periods of 80 days or more. The helium was then released by heating the solid salt and some 6 - 10 cu. mm (at N.T.P) of gas were produced which was measured with accuracy in the McLeod gauge. A temperature of 450° was required to drive out all the helium. By repeating the process at intervals of a few days, Dewar showed that the total volume of gas increased steadily with time.

In the first experiment the results indicated a value of 3.88×10^{10} alpha particles per sec per gm for the specific activity of radium and the second experiment gave 3.70×10^{10} alpha particles per sec per gm.(These are calculated from the rate of helium emission using the most recent values of the Loschmidt number).

The big disadvantage of Dewar's method was that no provision was made for removing hydrogen. Dewar himself pointed this out in the second paper. There may have been organic matter or water on the walls of the apparatus and in the salt which would have produced appreciable quantities of hydrogen under alpha particle bombardment. This experiment is one of the earliest and a high degree of accuracy is not to be expected.

Volume of helium.

(ii) Rutherford and Boltwood (Ref. 2.20)

This experiment was similar to that described above. The measuring instrument was a McLeod gauge calibrated in a similar manner. The quantities of radium salt and the periods of accumulation of helium were of roughly the same order. Boltwood and Rutherford, however, took considerable care to remove hydrogen from the helium. The gases were sparked with oxygen and passed together with oxygen over heated copper oxide, the excess oxygen and a certain fraction of the helium then being absorbed on charcoal at liquid nitrogen temperatures. The fraction of helium absorbed in the charcoal tube under standard conditions was determined in a calibration experiment. In one experiment Boltwood and Rutherford expelled the helium by heating the solid salt and showed that the build-up of gamma ray activity in the salt subsequently was what would have been expected had the radon been completely expelled. Therefore there is little doubt that the helium was also expelled from the salt. In a second experiment the radium chloride was dissolved in hydrochloric acid for 80 days and the helium removed by pumping under vacuum.

The average result of these two experiments (corrected using the most recent value of the Loschmidt number) was 3.3×10^{10} alpha particles per sec per gm.

The method is an improvement on that of Dewar in that contaminating hydrogen is removed and attention is given to the complete extraction of helium. However, the result is lower than most values and the question arises whether some helium was lost from the system. If recoiling radon nuclei escaped from the solid salt or diffused out of the solution, there would be a good chance of the alpha particles from the decay of this radon striking the walls of the vessel and being lost. Also some alpha particles from the outer layers of the radium salt would be brought to rest in the walls and so lost. As with Dewar's work this experiment is mostly of historical interest.

Helium evolved.

(iii) Gunther (Ref. 2.21)

This experiment bears a close resemblance to that which forms the subject of this thesis. The method of analysis used was that first used by Paneth and Peters and was capable of measuring 10^{-6} ml of helium with an accuracy of 1%. Gunther used a vessel of Jena glass which was filled to the top with radium solution. Radon was removed, then helium was allowed to accumulate for a period, after which it was swept out with electrolytic gas and analysed.

The radium used was standardized beforehand; it was sealed into an ampoule of the same wall thickness as that containing a standard sample. The two were then compared by the intensities of gamma ray activity.

The experiment was intended only as a check on the accuracy of the method which had been used for other half-life determinations. A value of 3.67×10^{10} alpha particles per sec per gm for the specific activity of radium was reached, but the fact that this was regarded as in good agreement with the value most widely accepted at the time (3.7×10^{10}) shows that the probable margin of error of Gunther's work was well over 1%.

The method of measuring helium was a great improvement on that of Dewar. Its further improvement by Glueckauf was the basis of the work to be described.

(δ) Advantages of the Helium Method.

The method, which was explored in this work, of measuring the volume of helium produced from a radium solution possesses a number of advantages over most of the methods used previously for the determination of the half-life of radium. These are as follows:

(i) A direct count is made of the alpha particles themselves in the form of helium atoms. The measurement is not dependant on any property of the emitted alpha-particles, their ionizing properties, their energy of emission, or their transfer of electric charge. Moreover no assumptions have to be made about the charge on a single particle, its energy or exact range, or its equal probability of emission in any direction. The only assumption is that an alpha-particle is a helium nucleus which on coming to rest will give a helium atom, and that its range in water is small (of the order of 0.01 cm).

(ii) The absolute measurements are simple volumetric ones. There is no counting device of uncertain and indeterminate efficiency.

(iii) Helium is very easily handled chemically and can be separated without great difficulty from other substances.

(iv) The technique of measuring micro-quantities of helium has been well established. It is possible to check most stages of the measurement to make sure that the apparatus is giving accurate results. The subjective element is not large, being involved only in observing deflections of a mirror galvanometer, in measuring a pressure difference with a cathetometer, and in setting various columns of mercury accurately to known heights.

(v) The measurement may be repeated indefinitely by repeated extraction of helium from the one radium solution.

(vi) The handling of active samples is cut down to a minimum. Once the radium is dissolved it need not be manipulated again.

There is no error introduced by the mounting of a sample on a support of any sort with the attendant difficulties of absorption and scattering.

(vii) The measuring section of the apparatus is not contaminated by radon or by recoiling nuclei.

CHAPTER 111

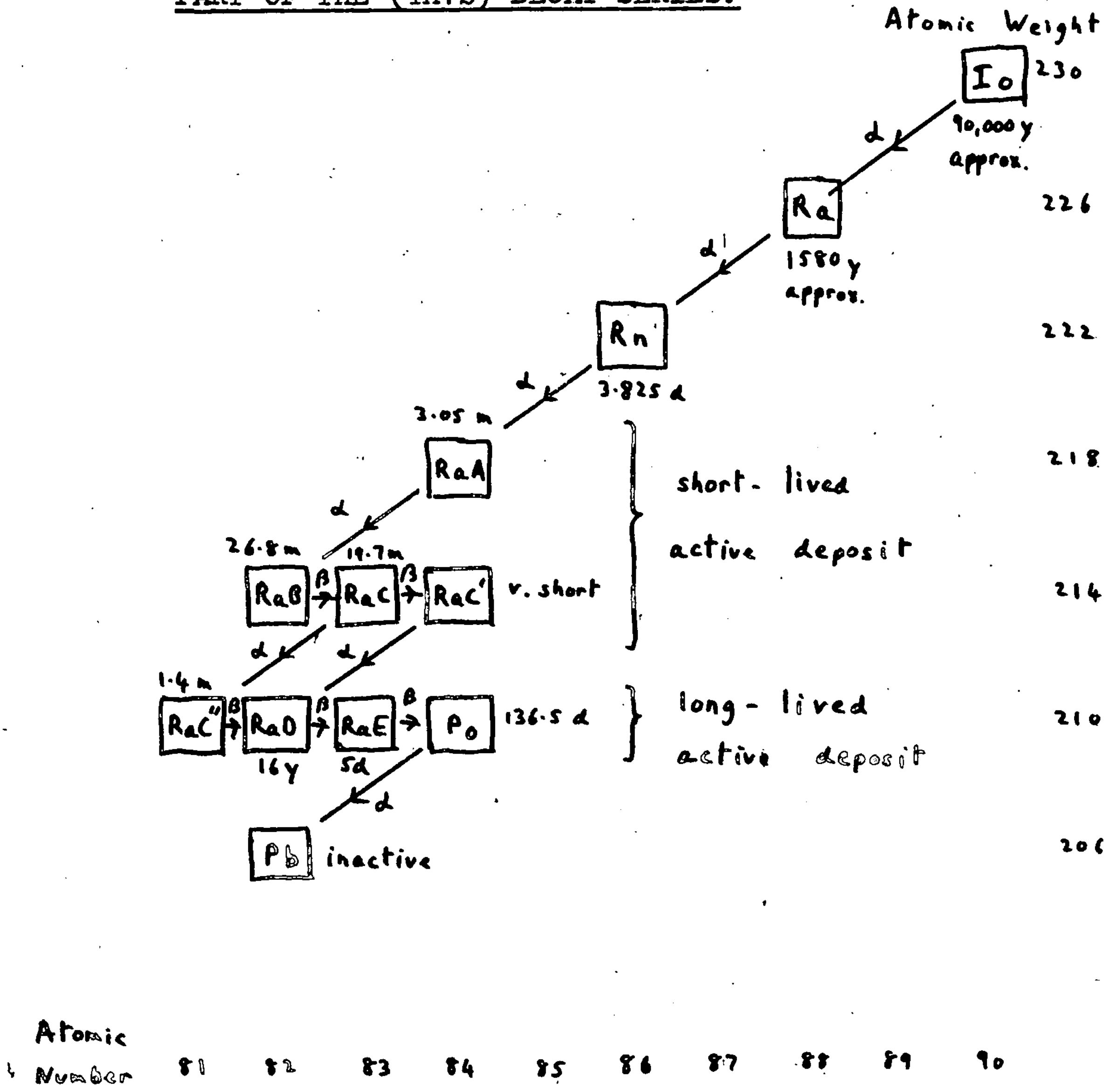
GENERAL OUTLINE OF THE METHOD.

The radium was contained in a solution of a suitable solvent, the volume of the solution being large enough to ensure that over 99.5% of the alpha-particles came to rest in the body of the solution. Radium chloride dissolved in dilute hydrochloric acid or radium sulphate in 95% sulphuric acid was used for most of the work. The solution was freed from radon and short-lived active deposit by blowing a carrier gas through the solution continuously for eight hours. Helium was then allowed to accumulate for a period of one or two days. The rate at which it accumulates is governed by the disintegration constants of the daughter products (which were all known with good accuracy), the mass of radium present (which had to be determined) and the specific activity of radium. At the end of the period of accumulation the helium was removed from solution by passing carrier gas and was measured in the apparatus described by Glueckauf, (Ref. 3.1), which is capable of measuring 5 x 10^{-7} ml of helium with a margin of error of less than 0.4%.

For convenience a table of the relevant portions of the uranium (4n+2) decay series is here reproduced:

TABLE 11

PART OF THE (4n+2) DECAY SERIES.



Radium D, radium E and polonium were removed before using the radium solution and because the half-life of Ra D is long, radium E and polonium did not accumulate in significant quantities during the course of the work. Radium D was effectively the end product, and there were no alpha particles due to polonium.

Radium on decaying gives first an alpha-active rare gas, radon, which then produces a short-lived product of effective half-life about half-an-hour, which in turn emits two more alpha particles and gives a long-lived product, radium D. The existence of a branched decay chain at this point does not affect the production of alpha-particles. The only members of the series which are conspicuously gamma active are radium itself and radium C. The gamma activity due to radium C is far more intense and has a greater penetrating power than that due to an equilibrium amount of radium. By the use of a lead screen of 1 - 2 cm thickness, the intensity of the gamma radiation due to radium (and all beta radiation) can be reduced to negligible proportions while still allowing an ionization due to radium C gamma rays that can be easily measured. This fact was used to check the completeness of removal of radon and short-lived deposit at various stages.

CHAPTER 1V

CONSIDERATION OF VARIOUS FACTORS AFFECTING THE ACCURACY.

(α) Removal of Radon (β) Bateman Factors
(γ) Maintenance of Radium in Solution
(δ) The Period of Helium Accumulation
(ϵ) Keeping the Radon in Solution
(ζ) Removal of Helium
(η) Correction for alpha-particle loss

(α) Removal of Radon.

In order to know what fraction of the helium produced in the solution in a given time was due to the α- decay of radium, it was necessary to know how much radon and short-lived deposit was present in the solution at any time. One might have started from equilibrium conditions; however the equilibrium was disturbed by each measurement and it would have required a month for equilibrium conditions to be re-established. It was better, therefore, to ensure that initially there was only radium and long-lived deposit present.

This was achieved by continuous removal of radon for a period of some hours; the removal was as rapid as possible so that the number of radon atoms decaying while still in the solution was very small. During this period all the shortlived deposit initially present decayed. No more short-lived deposit was formed in solution because the radon was quickly removed before any appreciable quantity of it could suffer decay. The effective half-life of the short-lived deposit is slightly over 30 min. so that a period of eight hours during which radon was removed was sufficient to allow the short-lived deposit to decay to negligible proportions. Radon was removed by bubbling a carrier gas through the solution at a steady rate. Earlier workers on this problem at Durham found that the retained gamma activity, due to radium C in equilibrium with radon fell to below 0.2% of the activity in equilibrium with the radium. This result was confirmed during this work, to within the limits of accuracy required, by drawing air through a radium solution placed at a convenient distance from a Geiger counter. The intensity of the gamma activity was followed. All other rays were cut out by the thick lead walls surrounding the counter. The intensity was plotted for two such experiments on semi-log plot (see Fig.3) and after seven hours had fallen in each case to less than 0.8% of the original, or 0.5% of equilibrium.

(β) "<u>Bateman Factors</u>".

As the daughter products of radium built up in the solution initially freed from them, they contributed an increasing number of alpha-particles to the total produced.

One of the important numerical factors which had to be calculated was that which expressed the ratio between the number of radium atoms decaying in a period of accumulation of any given length and the number of helium atoms produced in that period. The former term is what was required. The latter is what was measured. The ratio depended in a complicated manner on the half-lives involved. Since the formulae which gave the amounts of daughter products present were derived by Bateman (Ref 4.1) the factor was called the "Bateman factor" and was given the symbol β. It was derived as follows:

If the radium solution was initially quite free from radon and all short-lived deposit and contained N_0 atoms of radium, then $N_0 \lambda_0 t$ atoms of radium decayed in time t, where λ_0 is the radioactive constant of radium. If all these atoms decayed to long-lived deposit, we should have $4N_0 \lambda_0 t$ atoms of helium. But they do not; in fact there are N_1 atoms of radon present at time t, N_2 atoms of radium A, N_3 atoms of radium B, and N_4 atoms of radium C + C'. Each radon atom represents three atoms of helium not yet produced; each atom of radium A, two atoms of helium; and radium B and radium C each one atom of helium.

So, helium produced = $4N_0\lambda_0 t - 3N_1 - 2N_2 - N_3 - N_4$

But N_1, N_2, N_3 and N_4 are given by the Bateman formulae.

$N_1 = \frac{N_0\lambda_0}{\lambda_1}(1 - e^{-\lambda_1 t})$ where λ_1 is the decay constant of radon.

$N_2 = \frac{N_0\lambda_0}{\lambda_2}(1 - e^{-\lambda_1 t})$ since we can consider radium A to be in equilibrium with radon.

$N_3 = \frac{N_0\lambda_0}{\lambda_3}\left(\frac{1 - \lambda_1 e^{-\lambda_3 t} - \lambda_3 e^{-\lambda_1 t}}{\lambda_1 - \lambda_3}\right)$ where λ_3 is the decay constant of radium B.

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

where ${}_4$is the decay constant of radium C

Now λ_1 (Ra) = 0.0075545 hr^{-1} $\lambda_3 - \lambda_1$ = 1.54426 hr^{-1}

λ_2 (Ra A)=13.6355 hr^{-1} $\lambda_4 - \lambda_1$ = 2.10354 hr^{-1}

λ_3 (Ra B)=1.5581 hr^{-1} $\lambda_4 - \lambda_3$ = 0.55928 hr^{-1}

λ_4 (Ra C)=2.11109 hr^{-1}

Therefore helium produced = $N_0\lambda_0(4t - 398.38 + 398.37\,e^{-0.0075545\,t} - 0.01190e^{-1.55181t} + 0.004\,72e^{-2.11109\,t}$

For values of t greater than 5 hr, the last two terms become negligible and we have $\beta = 4t - 398.38 + 398.37e^{-0.0075545\,t}$

TABLE 111

TABLE OF BATEMAN FACTORS.

t in hours	β	$t\beta$ in hours	t in hours	β	$t\beta$ in hours
0	1	0	30	1.3073	39.2182
5	1.0478	5.239	50	1.4936	74.683
10	1.1021	11.025	70	1.6627	116.389
15	1.1552	17.3280	100	1.8878	188.782
20	1.2071	24.1413	120	2.0211	242.537
25	1.2588	31.44447	150	2.1994	329.904

The values of β required for the final measurements were calculated directly.

Now let us consider the case where radon was not completely removed for some reason, but a fraction x was retained. The daughter products would remain with it and the gamma activity due to radium C would remain at a fraction of the equilibrium activity (which could be found from the activity after a known time by use of a simple exponential function). Then a fraction x of the radium was in equilibrium with its daughter products and this part of the system produced $4x\lambda_0 N_0 t$ alpha-particles in time t. The remainder 1 - x had the usual Bateman factor. The "apparent Bateman factor", β' was therefore: $\beta' = 4x + \beta(1 - x)$

(γ) Maintenance of Radium in Solution.

If any of the radium was present in the solid state (as particles of radium silicate, for instance) then the radon would not have been able to escape as soon as it was produced and an indeterminate amount of radon and active deposit would have been present at the commencement of the period of helium accumulation. Moreover the helium produced in such particles might not have been able to escape, depending on the size of the particles. Again if the radium was not held in solution, it might have been deposited on the walls of the vessel, in which case the number of alpha-particles coming to rest in the walls would have been larger than calculated (see section η of this chapter). It was therefore essential that the radium be kept in solution; the ease with which this could be done with the various solvents used is discussed in Chapter V, section β.

(δ) Timing the Period of Helium Accumulation.

The length of time for which helium was allowed to accumulate was measured with accuracy. It was defined by the moment when removal of radon ceased and by the moment at which helium was removed after accumulation. The former was taken as the moment when flow of carrier gas was shut off, but the latter, the removal of helium, was more indeterminate. The helium was swept out by successive short flushings with the carrier gas and this operation might take 15 - 20 minutes. During this period helium was still being produced, most of which was swept into the measuring system during the last flushings. The end of the period of accumulation was therefore the <u>end</u> of flushing out the helium, but as a general rule two minutes were subtracted from this time to allow for the possible incomplete removal of helium in the last few minutes. If we allow for a possible indeterminacy of three minutes in the time, then a total accumulation period of 1200 minutes = 20 hours will reduce the indeterminacy to 0.25%. The periods actually taken were slightly under 48 hr and slightly under 96 hr.

(e) Keeping the Radon in Solution.

All the alpha-particles from the radon and the short-lived deposit had to be brought to rest in the solution so that the atoms of helium could be removed, because the helium resulting from any alpha particle coming to rest in the walls of the vessel would not be recovered at once. If any of the radon had been present in the vapour phase in the space above the solution, its alpha particles might have struck the walls of the vessel. Moreover the resulting short-lived deposit would have been deposited on the walls and half the alpha particles resulting from its decay would have been lost.

This effect was reduced to negligible proportions by freezing the solution or by arranging for the space above the solution to be reduced to a minimum. If the solution was frozen solid within, say 15 minutes of the end of the period of radon removal, the radon as formed in the body of the solution was unable to diffuse into the gas space. According to Hahn (Ref. 4.2) the rate of diffusion of radon in solid inorganic substances is very slow, although there is some evidence to show that diffusion occurs in barium nitrate, at least. But for present purposes it is quite negligible.

The effect was not appreciable during the 20 minutes which elapsed between melting the solution after helium accumulation and the end of the flushing-out of helium.

On the other hand if the gas space above the solution was small the proportion of radon in the vapour phase would also be small. According to Meyer (Ref. 4.3) the distribution coefficient, α , of radon between water and the vapour phase is 0.255 at 20° C. If the gas space was, say, 0.01 ml and the solution was 25 ml in volume then the proportion of radon in the vapour phase was 1/2500 x 0.255 = 1/625. In periods up to 100 hours the daughter products of radium contributed less than half the total alpha particles, the loss of alpha particles due to radon in the gas space is seen to be very small indeed.

(5) Removal of Helium.

It was clearly a point of importance that all helium should have been removed from the solution before the period of accumulation began, but if removal of radon from the solution was complete at this stage then all the helium would be removed also. It was likewise important to establish that all the helium was transferred into the measuring apparatus at the end of the period of accumulation. Therefore a normal 'flushing' was performed using the standard technique of seven successive portions of carrier gas, bubbled through the solution and then allowed to flow into the measuring apparatus. This helium was treated in the normal manner and as quickly as possible a second 'flushing' of the flask, exactly similar, was performed. One hour had elapsed between the two 'flushings'. These two portions of gas were passed through the measuring apparatus successively and the second sample was found to contain no more helium than would have been expected to grow in the hour that had elapsed, within the limits of error of the measuring system. This confirmed that there was complete removal of helium from the flask and also from the first section of the measuring apparatus. The experiment was performed on a number of occasions, including one during the final series of measurements.

(η) Correction for Alpha Particles Lost from Solution.

A correction could be made for the number of alpha particles lost by being brought to rest within the walls of the vessel. The range of the most energetic alpha particle in the decay series is 0.0088 cm approx. in water. 1/4 of the alpha particles from a layer of this thickness over the whole surface of the solution would be lost. The smallest bulk of solution employed was a cylinder of surface area about 40 sq.cm and volume about 20 ml, for most of the work the volume was about 30 ml and the surface volume ratio correspondingly smaller. The volume within this surface layer was 0.35 ml and one quarter of the particles emitted within this volume was lost, about 0.5% of the total. In fact the percentage loss was less than 0.5% since only the radium C' alpha particle has a range as large as 0.0088 cm. A correction could have been calculated for this effect that would have made the error involved quite negligible, but in fact there was no occasion to do so.

CHAPTER V.

PREPARATION OF THE RADIUM SOLUTION.

(α) Formation of a Precipitate in Aqueous Solution.

(β) Advantages of Various solvents.

  (a) salt flux.

  (b) sulphuric acid.

  (c) dilute hydrochloric acid.

(γ) Preparation of Solution.

  (a) Purification from silicate.

  (b) Purification from lead and polonium.

(δ) Method of Standardization.

(α) Formation of a Precipitate in Aqueous Solution.

Earlier workers on this problem (Ref. 5.1) had observed that a slightly gelatinous precipitate appeared in aqueous solutions of radium salts which were allowed to stand for any length of time in vessels made of soft (soda) glass. This precipitate is believed to have been largely radium silicate. The strongly ionizing radiations attacked the glass, hydrolysing the silicates, which then precipitated the insoluble radium silicate. Under these conditions it was not possible to remove radon completely from the solution. The evidence for this is the fact that there was always some short-lived deposit remaining, which could be detected by its powerful gamma ray activity. It was believed that the radon which was evolved from the solid radium salt was trapped within the solid phase and so was unable to escape. The earlier work also showed that an aqueous solution in contact with a borosilicate type glass, such as Pyrex brand glass produced no observable precipitate after several months in contact with radium solution. However,borosilicate glasses were known to be permeable to helium, as will be discussed later.

It was therefore desirable to consider the relative merits of various other types of medium in which a solution containing radium might be made. The three possibilities considered were: (a) a flux of some low-melting mixture of salts, (b) concentrated sulphuric acid, (c) aqueous solutions. The advantages and disadvantages of each possible medium, as revealed in these experiments will be discussed from five points of view. (i) the solubility of a radium salt, (ii) the completeness with which radon and helium could be removed, (iii) the volatility of the medium, (iv) the compatibility with the containing vessels, (v) the temperature changes involved.

(β) Advantages and Disadvantages of Possible Media.

(a) Mixture of Salts. Three mixtures were used, 'fusion mixture' (sodium and potassium carbonates), the eutectic mixture of 59% potassium chloride and 41% lithium chloride (m.p. 352° C.) and the sodium nitrite-potassium nitrite eutectic (sodium nitrite 65%, m.p. 219° C.). These were all solid at room temperature and had to be held in the molten condition for eight hours under a low pressure. A stainless steel tube was made in which this could be done, and small cylindrical crucibles containing the salts were introduced.

(i) Solubility of Radium. Little is to be found in the literature concerning three component systems of radium salts. However barium chloride was found to be soluble to the extent of several mg. per 5g in all the fluxes and radium salts generally resemble barium salts closely in chemical properties.

(ii) Extraction of radon and helium. Experiments were not carried as far as the investigation of this, but it is believed there would have been no difficulty. At the elevated temperatures employed flushing with carrier gas would have been unnecessary because convection currents in the melt would have provided sufficient stirring.

(iii) Volatility of medium. This depended on the type of flux. Carbonates dissociated at the high temperatures and low pressures involved, leaving oxides of sodium and potassium. Mixed chlorides and nitrites did not present this problem.

(iv) Compatibility with containing vessels. A chloride flux was strongly corrosive at its melting point even towards stainless steel tubes. Moreover all the fluxes showed a strong tendency to 'creep' out of metal containers, and after a long period at elevated temperature the bulk of the flux was found on the outside of the crucible and the base of the furnace. This property chiefly ruled out the use of salt fluxes.

(v) Temperature changes involved. Salt fluxes possessed the advantage that no freezing of the solution was required and there was no difficulty in keeping the solution solid during periods of helium accumulation. However elevated temperatures were required for the periods when the solution had to be liquid. There are few convenient fluxes melting below 400°C. At this temperature metal or Pyrex had to be used for the furnace. If metal, there had to be a metal to glass seal of some sort, protected from the heat, and a carrier gas would have been required which did not attack the metal at high temperatures. If Pyrex was used, the problem of the permeability of Pyrex to helium became far more acute. Largely owing to the 'creeping' difficulty work with salt fluxes was not carried very far.

(b) Concentrated sulphuric acid.

(i) Solubility of radium. Radium sulphate is soluble in small amounts in concentrated sulphuric acid. Trenner and Taylor found (Ref. 5.2) that the solubility of barium sulphate was over 10,000 times greater in 96% sulphuric acid than in 73% sulphuric acid and ascribed the increased solubility to formation of barium bisulphate. Underwood and Whittemore (Ref. 5.3) found that 79 x 10^{-6}g of radium sulphate was easily soluble in 100 g of 73% sulphuric acid and that thereafter the solubility appeared to increase sharply. By analogy with barium sulphate, this increase was ascribed to bisulphate formation. Radium sulphate was expected to be soluble to the extent of hundreds of mg per 100 g of 96% sulphuric acid. The concentrated acid had to be protected against any long exposure to the atmosphere, because it quickly absorbed water vapour and, becoming less concentrated, might have precipitated radium sulphate. The carrier gas had to be carefully dried by freezing out moisture in the cold-finger (see Fig.15 G) using a mixture of acetone and solid carbon dioxide.

(ii) <u>Ease of removal of helium and radon.</u> The controlling factor in estimating the ease with which helium and radon could be removed was the rate at which the gases could difuse to the gas-liquid interface of the bubbles of carrier gas. Owing to the greater viscosity of sulphuric acid, this diffusion was slower in sulphuric acid than in water. A rough check with a portable dosemeter on a solution of radium in concentrated sulphuric acid through which oxygen had been passed at a moderate rate for eight hours showed very little gamma activity (less than 1% of equilibrium) showing that radon had been more or less completely removed. However accurate measurements on this factor were not made, nor was a 'double' flushing' experiment carried out to check the completeness of sweeping out helium.

(iii) Volatility. This presented no trouble at all with concentrated sulphuric acid. Neither was there such a tendency to splash as there was in the case of water.

(iv) Compatibility with vessels. Solutions of radium sulphate in concentrated sulphuric acid had no effect on borosilicate glass of the Pyrex type. It is not known whether over a long period of time they would have attacked soda glass, since all the work involving sulphuric acid was performed in Pyrex vessels. Sulphuric acid could not, of course, be used in any system involving the use of mercury in the radium flask.

(v) Temperature changes involved. This was the major source of difficulty when using concentrated sulphuric acid. When a flask containing acid was slowly lowered into liquid nitrogen supercooling occurred. The acid did not crystallize in the usual sense but became more and more viscous as it cooled hardening finally to a glass which cracked with a sharp report. Trials with a thermocouple indicated that a temperature of - 106°C. was reached in the centre of the flask before all the acid had solidified. At first on cooling a layer of fine cracks appeared in the acid in contact with the glass. After a minute or two the fine cracks would gradually disappear and the acid toward the centre, which had been becoming more and more viscous, would show that it was solid by cracking with a sharp report. Further cracking occurred until the cold acid was a network of cracks. Apparently as each crack appeared there was a stress wave which passed through the acid. On several occasions despite the fact the acid was cooled very slowly these stress waves broke the glass of the flask. The breakage was not due to expansion of the acid, which contracts on solidifying as evidenced by a shrinkage depression on the surface of the finally frozen solid. Pear-shaped vessels were used to allow for gradual freezing from the tip upwards. Normally it was possible to lower such a vessel 4 or 5 cm into liquid nitrogen before breakage occurred, and one such vessel was frozen 30 or 40 times with success.

Various attempts were made to solidify the acid using a mixture of acetone and solid carbon dioxide. At the temperature produced by this mixture, the acid was no more than a viscous paste. Such a paste would probably not retain radon satisfactorily. Attempts were made to induce genuine crystallization. Various centres for crystallization were introduced, including a tungsten wire sealed into the base of the flask. The only successful procedure was vigorous scratching with a glass rod, which gave a crystalline solid melting at about - 30°C. The freezing point of slightly aqueous acid variess sharply with water content, but in no case does it reach a value below - 100°C. Many efforts were made to overcome this problem, but the only answer seems to lie in making a strong flask and testing it carefully before risking its use with radium solution. For this reason and also because an aqueous solution was preferable from the point of view of the final analysis to determine the total weight of radium, sulphuric acid was abandoned as a solvent.

(c) Aqueous Solutions. After study of other possibilities, work was resumed with aqueous solutions. Water still presented great difficulties but they were apparently not so great as those of other media. The 'floating-on-mercury' type of flask (See Chapter Vl section β) required the use of aqueous solutions.

(i) Solubility of radium. Radium chloride is easily soluble in water and dilute hydrochloric acid. In order to prevent deposition of active deposit in the solid state a normal solution of hydrochloric acid was used.

(ii) Extraction of radon and helium. This was more easily carried out than in the case of sulphuric acid. Experiments performed to check the completeness of the extraction have already been described (Chapter lV, sections ζ).

(iii) Volatility. This was a matter of considerable difficulty. Water is fairly volatile and the passage of carrier gas reduced the volume of the solution by two or three ml at every eight hour period. Fresh distilled water was added as needed, but any systematic error depending on the volume of the solution was difficult to estimate. Moreover, the mobile aqueous solution splashed very freely. The carrier gas entered the solution under a pressure of some 10 cm of mercury and left at a pressure of 3 cm or much less; so there was considerable expansion in passing through the solution. This resulted in large bubbles which often carried solution to the upper end of the flask.

(iv) Compatibility with vessels. As already pointed out, aqueous solutions of radium salts were quite compatible with Pyrex vessels but attacked soda-glass vessels over a period of time with consequent precipitation of radium silicate. It was possible to protect a soda-glass flask from attack by coating the inside with plastic or with an acid-proof varnish. This is what was actually done. The varnish darkened slightly in colour but showed no other outward signs of attack by radium solution.

(v) Temperature Changes Involved. To freeze an aqueous solution quickly required liquid nitrogen. There was no supercooling effect such as was observed with sulphuric acid, and the solution froze smoothly as the level of the liquid nitrogen bath was raised. Since water expands on freezing, it was advisable to use a pear-shaped vessel and to cool it gradually from the tip upwards. Once frozen, it could be kept in the solid state by surrounding it with a beaker containing chips of solid carbon dioxide. Which medium was most preferable depended to a certain extent on the type of flask used. Discussion of the question is therefore postponed to the end of Chapter VI.

(γ) Preparation of the Radium Solution.

(a) *Purification from silicate.* The radium as received was in various vessels which had been used in earlier work; the bulk of it was in the form of radium silicate. The silicate solids were transferred to a platinum evaporating dish and fumed to dryness with concentrated hydrofluoric acid. This procedure was repeated several times and the silicate was, at least in part, converted to fluoride.

$$\mathrm{Ra\,Si\,O_3 + 3H_2\,F_2 \qquad Ra\,F_2 + Si\,F_4 + 3\,H_2O}$$

Radium fluoride is only slightly soluble in water, so it was treated with concentrated hydrochloric acid to convert it to chloride. A certain amount of radium chloroplatinate was also formed from the attack of the platinum dish. Also it was found that the conversion of the silicate had not been complete. Therefore the hydrofluoric acid treatment was repeated and the resulting radium fluoride was converted to radium nitrate in the platinum evaporating dish. The excess nitric acid was evaporated, the solid residue was dissolved in water, transferred to a silica evaporating dish and converted to chloride.

Checking the various vessels with a Geiger counter showed that the bulk of the radium was still in an insoluble form. This did not have the appearance of the rather slimy silicate, but it proved to be soluble in concentrated sulphuric acid, this confirming the suspicion that it was radium sulphate. Since at this time the possibility of using sulphuric acid as a solvent was under consideration, the various radium residues soluble in concentrated sulphuric acid were collected together and dissolved in the minimum quantity of AnalaR 98% sulphuric acid. In this manner the activity which had clung tenaciously to various items of glassware was removed. The residues were evaporated in the platinum evaporating dish and the acid fumes were drawn off through a funnel to the filter pump. The solid sulphate residues were dissolved in the minimum quantity of concentrated acid and filtered through a number 5 sintered glass filter into the radium flask to be used.

When the work with concentrated sulphuric acid was abandoned, the sulphate was reconverted to a water-soluble form. The various sulphuric acid solutions were diluted with large amounts of distilled water and the precipitates separated using a centrifuge. These precipitates were dissolved in the minimum quantity of sulphuric acid and after removal of insoluble material, the acid was again diluted with water until the radium sulphate had been reprecipitated. This precipitate was separated, washed into a nickel crucible and gently dried. A little sodium carbonate was added together with lead sulphate as a carrier for polonium and radium D and the mixture was fused. It was hoped to get a clear melt, but after prolonged action there was still a certain amount of solid visible. The sodium carbonate and sulphate were dissolved in water and the residual solids, largely radium carbonate and other heavy metal carbonates, were transferred to a centrifuge tube. These heavy metal carbonates were treated with dilute hydrochloric acid. The portion insoluble in hydrochloric acid was taken back into the nickel crucible and re-fused with sodium carbonate. Finally the whole acid-soluble acid material was treated for removal of polonium.

(b) Removal of Polonium and Radium D. Before any accurate measurements were carried out it was necessary to free the radium from polonium and radium D which had accumulated in the course of the several years that had elapsed since the radium was last purified. The polonium and the radium D (which is a lead isotope) would have remained with the radium through the various chemical changes to which it had been subject. Since polonium is alpha-active and radium D produces polonium, a not-very-well-defined amount of extra helium would have been produced if either were present. They were separated from radium by precipitation with hydrogen sulphide. The pH of the solution in hydrochloric acid was adjusted to 0.5 using a suitable indicator and warm water saturated with hydrogen sulphide was added. A moderate sized black precipitate appeared. This precipitate was separated and the radium solution remaining was transferred to the radium flask for the final measurements. A larger amount of radium in the final solution would have been desirable. Very considerable amounts of radium were left behind at various stages owing to the incomplete conversion of sulphate to carbonate, and owing also to the carrying down of radium on the ~~polonium~~ lead sulphide precipitate. However there was sufficient radium to give measurable amounts of helium after two days accumulation.

Throughout the purification the radium was handled by means of pipettes made of drawn-out Pyrex 7mm tubing, fitted with rubber teats. The separations were performed in 10 ml Pyrex centrifuge tubes.

(δ) Intended Method of Standardization of Radium.

The original plan for measuring accurately the amount of radium in the solution was to use the radium from a secondary international standard which had been used in the atomic weight determinations of Hoenigschmidt. Then it was decided to compare a prepared sample with this standard source using gamma activities. The prepared sample would contain barium to bring the mass (and the self-absorption) to the same as that of the standard and would be sealed in an ampoule of the same shape and thickness. In this manner the errors normally associated with a gamma-ray comparison would be minimized.

However, before the end of the experiment, the standard sample became no longer easily available; and since time was short, it was decided to carry out measurements of the rate of helium evolution first and then to arrange for the solution to be analysed to determine its radium content. Facilities were available for doing this with a probable error of 0.5%. Accordingly at the end of the work the radium solution was to be transferred from the radium flask to a clean vessel and sealed to await analysis.

CHAPTER VI.

THE RADIUM FLASK.

(α) Material of the flask.
    (a) Pyrex glass.
    (b) Soda glass.
    (c) Plastic.
    (d) Metal.
(β) The Shape of the Flask.
    (a) Direct Freezing Type.
    (b) Floating-on-Mercury Type.
(γ) The Flask in Use.
(δ) Conclusions.

(α) The Material of the Flask.

(a) Pyrex glass. Borosilicate glasses of a type similar to Pyrex brand glass were known to be permeable to helium at room temperatures, but no figures were available at the start of the experiment. The possibility existed that helium, present in the atmosphere at a partial pressure of 2.5×10^{-6} atmos. would be present also in solution in the glass and would diffuse into the radium flask at significant rates. It was not known whether this would be a serious difficulty but preliminary experiments indicated that the leakage would be small enough to be negligible. A considerable series of experiments, including those with sulphuric acid, was based on the use of Pyrex for those parts of the flask which came into contact with radium solution. The junction with the soda glass which formed the rest of the apparatus was made with two ground glass cone-and-socket joints, made vacuum tight with Apiezon grease.

Subsequent experience indicated that the preliminary result must have been at fault, for an apparent leak developed in the flask. This leak continued when the flask was replaced by a sealed Pyrex socket, but disappeared when a soda-glass socket was used. Information became available during the course of the work concerning experiments carried out by Alpert and Buritz (Ref. 6.1) using the type of pyrex glass commercially available in the United States. They found that the solubility of helium in Pyrex is 10^{-2} ml (N.T.P.) per ml of glass per atmos. The diffusion coefficient at room temperature is 7.74×10^{-9} cm^2 per sec. The amount of a gas lost from a solid container into a vacuum is given approximately by $cs(kt)^{\frac{1}{2}}$ where c is the concentration of gas in the solid, s is the surface area of the solid, k the diffusion coefficient of the gas in the solid and t the time. Assuming the flask has internal surface area 200 sq.cm and a time of 50 hr has elapsed, we find that $200 \times 10^{-2} \times 2.5 \times 10^{-6} \times 8.5 \times 10^{-5} \times 7 \times 60 = 1.76 \times 10^{-7}$ ml helium can be expected. This is approximately the magnitude of the leaks found. This quantity of helium, is far from negligible for our purposes, and since it would exert a partial pressure in the flask much less than the partial pressure of helium in the atmosphere, permeation would continue at much the same rate for a long period.

The access of helium to the outside of the flask could be prevented but it would have taken at least a month for all the helium already dissolved in the glass to diffuse through. An attempt was made to speed the diffusion of the helium through the glass by holding the flask at a temperature of 200°C. in a bath of glycerine while preventing the air from reaching the outside of the flask. The flask was continuously evacuated on the inside. After four days of this treatment, helium was still found to be diffusing into the flask on standing. The gamma activity of the flask was found to be negligible, ruling out the possibility of the helium being due to residual radium in the flask. At this temperature, according to the American figures, the helium ought to have been removed within one day, but the difference may be explained by the difference between British and American Pyrex.

A Pyrex flask could only be used if access of atmospheric helium to the glass were prevented by coating the outside with varnish (which would almost certainly crack on freezing), immersing the flask in liquid (which could not be frozen at all), or jacketing with a soda-glass vessel, in which case the intervening space would need to be filled with some conducting substance which would not contract or expand unduly; a liquid such as n-pentane suggests itself. In any case Pyrex of suitable thickness contains a quantity of helium in solution which could only be removed by evacuating the inside of the vessel for at least a month. Such a procedure is by no means impossible but a less tedious method would be preferable.

(b) Soda-glass. Soda-glass was for practical purposes impermeable to helium. Paneth, Petersen and Chloupek (Ref.6.2) found that soda-glass after exposure to air dissolved 2.5×10^{-6} ml Helium (at N.T.P.) per g of glass, which was equivalent to 6×10^{-6} ml per ml of glass, or /31.5 ml /ml / atmos (for low He pressures). This solubility is greater than that of Pyrex. It is the low diffusion constant that makes soda-glass for practical purposes impermeable to helium. With the same formula as used above and the value 2×10^{-12} cm^2 per hr for the diffusion coefficient (Paneth and Peters, Ref. 6.3) it was found that 8.4×10^{-11} ml (N.T.P.) of helium would permeate into the flask in 49 hours. This was quite negligible The difficulty was that soda-glass was subject to attack by aqueous radium solution as has already been described. It was possible to prevent the soda-glass from attack by lining it with some inert protective substance. This was in fact done, the following conditions being fulfilled; the lining had to adhere closely to glass, it should not absorb radon or helium, it had to be resistant to attack by ionizing radiation or normal hydrochloric acid, it had to be easily applied to the inside of a rather complicated vessel. A fifth condition was imposed at first, that it should not crack under the stress of sudden cooling. This requirement was far too stringent and was avoided by using a floating-on-mercury type of flask (see next section).

Polythene was the first material tried for the inside coating and a number of tests were carried out with it. It could not be deposited from solvent, the thin layer cracked as the solvent dried out, and it adhered very badly to the glass. An even, rather thick coat could be applied by melting the polythene and allowing it to run round the inside of the flask, Charring was marked and most varieties of polythene began to decompose at temperatures below that at which they flowed freely even when melted under vacuum. A reasonable coat was obtained but it did not adhere closely to the glass and peeled off in use.

A special acid-proof varnish,"Sealocrete TF 19" was then used. By running this varnish around the side of a test-tube and baking it at 120°C. a good hard finish could be obtained. The varnish was then applied to the radium flask with complete success. To test the adhesive qualities of the varnish, the coated test tube was shaken with dilute hydrochloric acid and mercury in a mechanical shaker for two hours, and the varnish was unaffected. In actual use the varnish was also to all outward appearances unaffected apart from a slight darkening.

However, nothing is known about the surface absorbtion of helium, radon, and/or radium ions on this varnish coat. Some such phenomenon may account for the rather curious results finally obtained.

The possibility of preventing radium solution from reaching the soda-glass by placing the solution in a small vessel of Pyrex, plastic, or metal was considered. The latter would have been enclosed in a helium-tight, pressure withstanding vessel of soda glass. The possibility was dismissed because an aqueous solution would have distilled out of the inner vessel when the outer vessel was cooled, and the contents of the inner vessel could not have been frozen when surrounded with an effective vacuum jacket.

(c) Plastic. A radium flask made entirely of plastic was considered. The rather scant available evidence indicated that most plastics were impermeable to helium, and unattacked by aqueous acids or ionizing radiation. However polythene, at least, was very brittle at low temperatures. A short length of polythene tubing containing concentrated sulphuric acid was cooled until the acid was solid. The tube then shattered suddenly and spontaneously. It would have been possible to avoid the necessity for freezing by using a 'floating-on-mercury' type flask but this would have required a flask of a design too complicated for execution in plastic in the time available.

(d) Metal. No experiments were actually carried out with metal flasks, but most metals are impermeable to helium. The effect of the radium solution would have been unpredictable. Metals which ordinarily would resist N hydrochloric acid might not have done so under the influence of alpha-particles, although one would expect stainless steel, chromium, or platinum to resist attack. Finally it was helpful to be able to see the solution in order to control the flow of carrier gas and to know when the solution was solid.

(β) Shape of the Radium Flask.

(a) Direct Freezing Type. When it was required to freeze the solution, a pear-shaped vessel was used with a fairly narrow tip pointing downwards. The solution could then be frozen from the bottom upwards and any expansion could be accommodated. This type was used in two main modifications, each designed to permit, if required, the use of Pyrex glass for the flask itself. They are shown diagramatically in Fig.4. In type 1 the ring-seal was part of the fixed portion at A; in Type 11 it was part of the removable portion at B.

In Type 1 the carrier gas was led in at C, and the ring-seal A was in soda-glass. The gas passed down the inner bubbler tube which contained a soda-Pyrex graded seal, D. (This replaces the narrow cone-and-socket used at first). The lower part of the bubbler, E, could be made of Pyrex. The flask itself, which could be of Pyrex if necessary was attached to the fixed part of the apparatus by a ground glass cone-and-socket, F. The gases on leaving the flask passed through this joint and up the side-arm G. Alternatively the side arm could rise from the shoulder of the flask as shown in Type 11. In this case a further cone-and-socket joint would have been necessary. The volume of the flask was about 100 ml and contained radium solution up to the level X. When water was the medium, the volume of the flask could conveniently have been larger than 100 ml and the neck below F longer than shown to accommodate bubbles and to prevent solution reaching the Apiezon grease on the ground glass joint.

In Type 11 the carrier gas was led in at H. The flask and the ring-seal were made in one piece and could be of Pyrex if required. They were attached to the fixed part by a ground-glass joint at J. The side-arm K, could emerge from the neck below B or, as in this sketch, be aligned so that solution might be removed directly with a pipette. The side-arm was joined to the fixed part of the apparatus at L.

Type 1 possessed the advantage that, should the flask have cracked under the stress of freezing water or sulphuric acid, it was comparatively simple to replace. Type 11 dispensed with the difficult graded seal which was a source of mechanical weakness, and with the joint F which was liable to be splashed with solution.

All the joints were made vacuum-tight with Apiezon grease.

A tap controlled the inflow of carrier gas and another tap the outflow. There was a small plug of glass wool in the outflow limb to block any fine acid spray, which might attack the grease of the outflow tap. Two alternative designs of bubbler tip are shown in diagrams 111 and 1V. These were designed to cause as much stirring of the solution as possible, which was particularly important when sulphuric acid was the solvent. Type 111 had open ends at P and Q and it was hoped that solution would be drawn in at Q on the principle of t the 'pneumatic lift'. It did not stir the solution very effectively. In Type 1V the bubbler tip was simply set off to one side of the flask and drawn out to as fine a point as possible to give small bubbles, which were desirable in order to present the maximum surface area for the escape of radon. This produced a rapid circulation and was adopted as the best design.

(b)'<u>Floating-on-Mercury' Type.</u> If soda-glass was used and protected from attack with some sort of varnish, considerable danger of cracking the varnish was involved whenever the solution was frozen. Now, as was mentioned in Chapter 1, section 2, the reason for freezing the solution was to keep the radon in the space above the solution to negligible proportions. It was further shown that this could also be done by reducing the gas-space above the solution to 0.1 ml approx. By floating the radium solution on a column of mercury, the whole solution could be raised to the upper end of a closed flask and the gas space thus reduced. The upper end of the flask could be closed with a tap. The mercury could then be lowered again before the flushing-out process, and in this manner the solution could be handled at room temperature throughout. Moreover the carrier gas could be admitted through the side of the flask below the level of the mercury, thus dispensing with the problem of coating the bubbler tube with varnish.

The design of this type of flask, which was the one used in the final measurements, is shown in Fig.5. The carrier gas was admitted through the tube A and was controlled by the tap B. It passed through a capillary tube C and was admitted through the bottom of the flask to a small bubbler tip D. The level of D was marked on the outside of the flask so that mercury should never be lowered below the level W. The mercury flowed in through a capillary tube E and was controlled by a mercury vessel which is not shown. In the lowered position the top of the radium solution was at the level X. The large volume above it was to deal with the size of the bubbles as they expanded to meet the low pressure on the outlet side. The first few bubbles had to expand into a nearly perfect vacuum and there was a very marked tendency for them to carry solution right up to the tap, F. The upper position of the mercury was at level Y and the top of the solution was then at level Z. leaving a volume of about 0.1 ml. The gases when removed passed out through the ground-glass joint G. The whole of this flask was made of soda-glass; it was coated on the inside from the tap F to the level W with Sealocrete varnish. Distilled water was introduced when needed through G and the solution could finally be removed through G. The volume of the solution varied from 30 ml to 20 ml and the total volume of the flask was about 150 ml.

(γ) The Flask in Use.

At the first use of this flask a slight cloudiness was noticed in the solution. This was ascribed to calomel, Hg_2Cl_2, produced by the interaction of mercury and N hydrochloric acid in the presence of oxygen which was being used as carrier gas. Test-tubes of mercury and normal hydrochloric acid were taken, various agents were added to prevent oxidation and then oxygen was bubbled through. No suitable agent was found which prevented attack. With perchloric acid the effect was the same, ruling out the possible intermediate formation of chlorine. A control experiment with distilled water gave no cloudiness. The reaction was formulated as:

$$4H^{+} + O_2 + 2Hg \rightarrow Hg_2^{++} + 2H_2O.$$

The oxygen of the carrier gas had therefore to be replaced with an inert gas of similar physical properties. Argon was chosen and a trial using argon, mercury and dilute hydrochloric acid showed no cloudiness. The possibility remains that mercury might have been slowly atacked under the influence of ionizing radiation even without O_2 present.

With this type of flask four successful measurements of the rate of evolution of helium from a radium solution were carried out. The results will be given in Chapter V111. It was found that in use there was a considerable tendency for the mercury to form a coarse emulsion with the solution, The mercury at the interface with the solution formed droplets which were closely packed together but apparently contained a certain amount of solution in the interstices. When the mercury was raised these droplets did not remain on the top but were drawn to the sides of the flask where they remained below the general level of the mercury. What volume of solution was trapped in this process, is not known, but the apparent volume of solution in the interstices was small.

At the end of the experiment the radium was removed by means of a long narrow pipette. The inside of the flask was washed as completely as possible using several successive portions of distilled water. When the residual activity of the flask was checked a month later, it was found that a large portion of the total gamma-ray activity was still associated with the flask. This indicated that the radium was still present, either on the surface of the mercury in the form of an emulsion, adsorbed on to the surface of the varnish, or possibly as radium silicate due to some unobserved breakdown of the varnish. This finding made it impossible to determine the amount of radium which had been present in solution.

(f) Conclusions Concerning the Flask and the Solution.

In view of the observation just mentioned it was concluded that the floating-on-mercury type of flask was not the best one. At the time it was adopted it seemed the best short-term answer to the problem but it gave rise to several difficulties in practice. These were: (i) The emulsifying effect at the mercury-solution interface which meant, even if the solution in the interstices of the mercury droplets was completely freed from helium and radon at the right moments, that a larger proportion of the alpha-particles than was calculated struck the glass walls of the vessel and were lost.

(ii) The unknown surface properties of the varnish, including the possibility of surface absorption of radon or radium ions and the possibility that at some point or other it had broken permitting contact of solution with glass. The likelihood that the latter had occurred was strengthened by the impossibility of removing radium from the flask and the nature of the systematic errors in the final results.

(iii) The close proximity of a tap to the radium solution, involving splashing of radium solution on to the tap grease and the possibility of small shreds of tap grease falling into the solution.

(iv) The necessity of using argon, which involved removing large amounts of hydrogen on the fractionating column. (see Chapter Vll, section ε).

(v) The possibility of attack on the mercury by the acid even without the presence of oxygen, an attack which might well have been promoted by the ionizing radiation.

If, in spite of this, work should be carried out using this type of flask, the following minor points may be noted.

(i) A preliminary experiment should be performed in which a radium solution is left in a varnished vessel for some time and then removed with thorough rinsing in order to determine whether any radium or any daughter products are absorbed on to the varnish.

(ii) The bulk of the radium solution should be as large as practicable (at least 30 ml) and should be kept as nearly constant as possible by adding water before every measurement.

(iii) The space above the solution should be greater, widening towards the top, in order to break up bubbles carrying radium solution up towards the tap; but at the lower end the tube should be narrower than in the flask used in order to ensure that solution near the walls is properly flushed out with carrier gas.

(iv) The line of the outlet tap and the ground glass joint above it should be slightly angled so that when radium solution is removed from the convex mercury surface it can

be taken from the side of the flask using a straight pipette.
(v) The total pressure on the outlet side of the solution should be kept at 5 cm of mercury during all bubbling. This would effectively reduce splashing.

If the floating-on-mercury flask is not to be used, we are again faced with the wider range of possibilities. For convenience they are tabulated here, with a note indicating the carrier gas required (other things being equal) oxygen is to be preferred) and the principal difficulties involved in their use.

TABLE IV

POSSIBLE COMBINATIONS OF FLASH AND SOLVENT WITH CARRIER GAS TO BE USED AND MOST IMPORTANT DISADVANTAGES

Solvent Material of flask	H_2SO_4 (freezing)	Water (freezing)	Water (floating-on-Hg)
Pyrex	O_2 Permeability to He	O_2 Permeability to He	A Permeability to He
Pyrex, coated on outside	O_2 cracking of coat Time of degassing	O_2 cracking of coat Time of degassing	A Time of degassing Proximity of tap
Pyrex, soda jacket, pentane	O_2 Slowness of freeze Time of degassing	O_2 Slowness of freeze Time of degassing	A Complicated shape Time of degassing
Soda	O_2 Possible attack	O_2 Attack	A Attack
Soda, coated on inside	O_2 Cracking of coat	O_2 Cracking of coat	A Absorption; USED Proximity of tap
Plastic	O_2 Cracking	O_2 Possible cracking	A Complicated shape
Metal	A Probable attack	A Possible attack	A Possible attack Complicated shape

It will be at once seen from Table lV that not all the above possibilities have actually been investigated in this work. Experiments were carried out only on those which seemed at the time most promising, indicated by heavy rectangles. Of the other possibilities the following seem most worth following up, in this order.

(i) Concentrated sulphuric acid solution in a plain soda flask might be used. It is not yet established whether or not soda glass is attacked by radium in concentrated sulphuric acid. Probably the incréased hydrogen ion concentration would make the hydrolysis of silicate more rapid than in water, but would suppress the concentration of silicate ion. If soda-glass is not attacked by sulphuric acid solution the problem becomes much more tractable. The remaining problem would be the stresses occurring on sulphuric acid on solidification. This problem is not insuperable. A spherical vessel of a good thickness of soda-glass (which is somewhat tougher than Pyrex) would not break so easily as those used in this work. Alternatively acetone and dry ice might be used as a cooling mixture. The rate of emanation from sulphuric acid cooled to a viscous paste by this mixture would probably be too high, but the point may easily be checked.

(ii) A plastic flask containing aqueous solution and cooled in a mixture of acetone and dry ice might be used. Available plastics might all turn out to be too brittle at this temperature but again the point is worth checking. The shape of the flask would need to be fairly simple.

(iii) A metal flask would probably be susceptible to attack by dilute acid in the presence of ionizing radiation. However stainless steel, chromium or platinum would be likely to resist attack. Argon would be used as carrier gas.

(iv) The fourth possibility has already been mentioned. A Pyrex flask completely surrounded by a soda-glass jacket. The intervening space would be filled with n-pentane, which would not freeze at the low temperatures to be employed. A small vapour space above this liquid would allow for differential contraction between the two vessels. Either aqueous or sulphuric acid solution could thus be used. However, the flask would require a long period of degassing from within before use, and a considerable period after any exposure of the inside to atmospheric helium.

With the exception of this latter suggestion, none of the methods involving coating Pyrex or soda glass either outside or inside really commend themselves. They require the use of the floating-on-mercury flask and present their own problems of adhesion, surface properties, breakdown of coating etc.

Finally mention should be made of other possible forms of solution. Various barium compounds, e.g. the chlorate, are soluble in various organic solvents, but they are mostly ionizing solvents and volatile, and would offer no advantages over water. Mixtures of inorganic salts, with which some work has been done, offer a good alternative if they can be so melted in a small crucible inside a steel furnace that no creeping occurs. A graphite crucible and a chloride flux (nitrite would probably oxidize a graphite crucible) are suggested as a result of the preliminary investigation into the salt-flux method.

Another possibility which has not yet been explored is to dissolve radium metal in mercury to form radium amalgam. The high stopping power of mercury for alpha particles would mean that only a small volume of solution would be necessary. The carrier gas would probably be argon and would have to be free from water vapour and oxygen (to prevent oxidation of the amalgam). It would be possible to dissolve sodium, which would be preferentially attacked, in the mercury, or to build a sodium-amalgam bubbler in the tube leading from the carrier gas system.

CHAPTER V11.

MEASUREMENT OF THE HELIUM.

(α) General Outline of Measuring Apparatus.

(β) Radon Traps.

(γ) Circulating System.

(δ) Fractionating Column

(ε) Delivery Rate of Fractionating Column.

(ζ) Pirani Gauges.

  (a) General Description.

  (b) Theory.

  (c) Fore-Space.

  (d) The Gauges.

  (e) Electrical Circuit.

  (f) Galvanometer Scale Correction.

  (g) Measures Taken to Combat Unsteadiness.

(η) Calibration System.

  (a) Earlier Design.

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  (c) Procedure in Using the McLeod Gauge.

(θ) Carrier Gas System.

(ι) Experiments with Air Samples.

(κ) Improvements and Suggestions.

(α) General Outline of the Measuring Apparatus.

The method used for measuring the helium is described by

Glueckauf, (Ref. 3.1) and was used by Chackett, Wilson, Reasbeck, Wardle and others. (Ref. 7.1). A block schematic diagram of the whole apparatus is given in Fig.6. The carrier gas system contained some ten litres of oxygen or argon. This gas was passed through the radium solution and through the radon traps where radon and water vapour were condensed. The carrier gas was either removed immediately by way of the secondary vacuum pump, or let into the circulating system where (if oxygen) it was circulated over a hot paladium tube in order to burn the hydrogen which was produced in the radium solution.

The remaining gases, oxygen or argon, hydrogen, nitrogen, helium and neon were pumped into the so-called 'fractionating column' where helium was separated from the other gases. The principle of the fractionation depended on the fact that oxygen, nitrogen and argon are quantitatively adsorbed on charcoal at liquid nitrogen temperatures. Of other gases helium is least adsorbed, neon somewhat more strongly, and hydrogen more strongly still. When a mixture of helium and neon was in contact with charcoal at liquid nitrogen temperature the ratio of helium to neon in the gas space in contact with the charcoal was greater than the ratio of the two gases adsorbed on the charcoal. By adsorbing and desorbing a mixture of gases in a series of these charcoal-containing tubes, differential separation could be obtained. Glueckauf showed that by using 12 units of the dimensions of those used in the present study, 99% of the total helium introduced, contaminated by only 1% of the total neon introduced could be delivered into a large vessel at the end of the column. From this large vessel the helium was compressed into a short length of tubing referred to here as the 'Pirani fore-space'. This section was then connected to a Pirani-Hall low-pressure gauge and the effect on the temperature of a heated wire filament determined. A known volume of pure helium was similarly delivered into the Pirani fore-space from the calibrating system. Comparison of the effects on the resistance of the Pirani gauge gave a measure of the unknown quantity of helium.

The entire apparatus (with one or two exceptions) was built of soda-glass through which helium does not permeate to any appreciable extent and is not permeable to helium. (Ref.6.1, 6.2, 6.3). This is only true of soda-glass which is not devitrified. Old soda glass, particularly if it has been worked, is liable to devitrification and these patches of glass are then markedly permeable to helium. A mercury vapour pump of the diffusion type backed by another of the condensation type, produced a vacuum which was believed to be between 1 and 3 x 10^{-7} mm of mercury. The mercury vapour pumps were water cooled and heated by 150 watt electric coils and were backed by a rotary oil pump. The gases were usually controlled in the apparatus by raising and lowering columns of mercury in various vessels, using a secondary vacuum provided by another rotary oil pump.

Each section will now be described in detail.

(β) The Radon Traps.

The gases issuing from the radium flask contained:

a large proportion of oxygen or argon as carrier gas,
helium from the alpha-particles and any helium present as impurity in the carrier gas or from air leaks,
neon from impurity in the carrier gas or from air leaks,
radon from the active solution,
hydrogen from the action of ionizing radiation on water or sulphuric acid,(Each alpha particle might produce up to 10,000 molecules of hydrogen),
nitrogen from impurity in the carrier gas or possible air leaks,
a considerable amount of water vapour, if an aqueous solution was being used.

Radon was condensed at low temperatures without removing the helium or the oxygen. The most convenient freezing agent available was liquid nitrogen. In a preliminary experiment a small sample of active solution and three simple finger traps in series were used. An appreciable proportion of the radon passed the first trap. The traps were then filled with soft-glass wool to prevent rapid passage of the gas and it was found that radon was practically completely absorbed in the first trap. In regular use the first radon trap (D in Fig.7) consisted of a tube 2 cm in diameter and 15 cm long. The gases were led in through a length of 7 mm tubing passing through a ring-seal at the upper end of the trap and were led out through a side-arm of the same diameter. The trap was packed loosely with glass wool. Constrictions were made in the inlet and outlet tubes (at F) and after each eight-hour period of radon removal or each flushing out of helium the tube was sealed under vacuum at these points and stored until the radon decayed.

After passing the radon trap the gases were led through a guard-tube which was simply a U-tube (E), packed with glass wool and immersed in liquid nitrogen. On two or three occasions this tube was removed immediately after passing radon through the system, and tested with a Geiger counter. It showed no significant gamma activity, thus showing that the finger trap was completely removing radon. The guard-tube was not replaced every time, but was simply allowed to warm to room temperature before the finger trap was sealed. Any radon in the guard-tube would distil back into the finger trap. In any case the passage of small amounts of radon into the vacuum system would have no permanent effect since the short-lived deposit would quickly decay, and the growth of any significant amounts of long-lived deposit would require exposure to radon for a very considerable period of time.

When aqueous radium solutions were being used, sufficient water distilled from the solution to block the finger trap with ice. During the long period of radon removal another trap G was inserted between the radium flask and the radon trap. This was 3.7 cm wide and 15 cm long and was not packed with glass wool. The gases were led in through the side arm so that ice forming would be less likely to block the tube. The lower half was cooled in liquid nitrogen and the tube was sealed and removed every time radon had been passed through it. No activity was detected in this tube after it was sealed. This arrangement prevented any blockage with ice.

To prevent any undue bubbling and splashing in the radium flask, a few cm gas pressure was maintained on the exit side of the radium flask and in the traps. This had to be less than 15 cm of mercury to prevent condensation of oxygen in the traps cooled by liquid nitrogen. The permanent pressure was obtained by the use of a bubbler, a U-tube, (H), containing a few ml of mercury in the tube leading to the secondary vacuum system, J, through which gases were passed during the eight-hour period of radon removal. (By using the secondary vacuum system for this purpose, the main vacuum system could be used to evacuate the rest of the apparatus.) The bubbler was protected by a tap (K in Fig.7). A bend in the tube above the bubbler (L) served to hinder the splashing of mercury into the secondary vacuum line. A similar bubbler was formed by the ventil (B in Fig.8) leading from the radon traps to the circulating system. These devices maintained a permanent pressure of some 3-4 cm on the outlet side of the radium solution. This pressure was quite sufficient for sulphuric acid solutions but aqueous solutions required a pressure of 5-6 cm which could not be maintained with the simple mercury bubbler.

This section of the apparatus also contained a by-pass tube, (Fig. 7,M) by which carrier gas could be led directly into the measuring system for various purposes. The carrier gas was let into the system from its store vessels at point I, by means of a control tap, N, and a mercury bubbler, O, and was led into the radium flask through S. The pressure was observed on a manometer P, not shown. The system was evacuated through the vacuum line Q. (A) leads to the rest of the measuring system. R is the mercury vessel needed for the floating-on-mercury type of flask (Chapter Vl,Section β).

(γ) The Circulating System.

The purpose of this section of the apparatus was to remove the hydrogen which was produced in the radium flask. The hydrogen was combined catalytically with a large excess of oxygen by circulating the gases over a heated palladium tube.

The system is shown diagramatically in Fig.8 . The whole formed a closed circuit of tubing into which the gases came from the radium section at A. With the mercury in the position shown the ventil at B acted as a non-return valve. The carrier gas as it came into the system, was adsorbed on the charcoal in U-tube E, which was cooled in liquid nitrogen. The ventils B and P, the by-pass Q, and the tap O were shut and E was warmed to room temperature. The resulting depression of the mercury in the Toepler pump, K, gave a measure of the amount of carrier gas used. A circulating pump, C, drove the gases round the system in the direction of the arrow. The palladium tube, electrically heated, is shown at G. The finger trap H was not used since the quantities of water vapour produced were small. After the gases had circulated for 20 min, the ventil I was shut, and the tap O opened cautiously. N, the first charcoal tube of the fractionating column, was cooled in liquid nitrogen, K was used as a Toepler Pump and M was a glass plunger holding up mercury and acting as a non-return gravity valve. The bulb of the Toepler pump was large enough to ensure that virtually all the gases would be transferred in 15 operations. The mercury was raised to the float-valve at S to minimize the volume associated with the first charcoal tube of the column. The circulating system was evacuated through the tap R and the ventil P before use. The tube which by-passed the fractionating column entered this section at Q, and was normally filled with mercury.

(δ) The Fractionating Column.

The theory of the separation of helium from neon has been fully discussed by Glueckauf (Ref.3.1) and there is no need to repeat it here. The experimental arrangement consisted of twelve units, one of which is shown diagramatically in Fig.9. The units were arranged alongside one another in a direction perpendicular to the plane of the diagram, the tube at P joined the tube of the unit before corresponding to Q, and the tube Q to the tube of the following unit corresponding to P. All the vessels corresponding to A were joined together at a point corresponding to side-arm F and were controlled together from a common mercury reservoir at G which is not shown. Similarly the B vessels were joined at H.

C was a U-tube containing 2.5 g of activated charcoal. The gases helium, neon and hydrogen flowed into it through P, with the mercury raised in both vessels to the level Y. The mercury in A was then lowered to the level X. This level was controlled automatically by a spring loaded valve between the taps controlling the mercury vessels and the vacuum line. A volume A of about 75 ml was exposed to the charcoal and the mixture of gases flowing into it was enriched somewhat in helium. The mercury was then raised to the level Y in A and lowered to the level X in B. This acted like a small Toepler pump sweeping the gases into space B. The mercury was then raised to level Y in B, driving the gases through Q to the next charcoal tube. At the same time the mercury was lowered in A to receive the next portion of gas. Glueckauf states that the equilibrium distribution of gas between charcoal and gas-space is reached within 5 sec. One minute is required for the whole cycle. The ball bearings at D and E acted as float valves to prevent mercury being driven in to the charcoal tubes. Every day before use, the charcoal tubes were baked at 150° C. under vacuum for periods of 20 min until a good vacuum was obtained.

(ϵ) Delivery Rate of the Column.

The amount and composition of the gas delivered into a reservoir of large volume at the end of the fractionating column after every operation of the column could be calculated from theory, but in practice it was determined empirically. An air sample (containing small percentages of helium and neon) with excess carrier gas was brought into the first charcoal tube. The carrier gas remained there, being for practical purposes quantitatively adsorbed. After 12 operations the first portions of helium reached the end of the column. There should be no gas delivered in fractions 1-12. Any gas in these fractions denoted incomplete evacuation of the column beforehand. If the amount of gas delivered by each successive operation was recorded, it was found that this rose to a maximum and then fell to a minimum at operations 25 and 26.

This gas was almost entirely helium. Further operations delivered more gas, almost entirely neon. Passage of the neon through the column could be speeded by removing the liquid nitrogen baths from the charcoal U-tubes after the last of the helium had passed that point and allowing the tubes to warm. The first charcoal tube was made slightly longer than the others so that it could still dip into a nitrogen bath when neighbouring tubes in the same bath were no longer immersed. This retained the carrier gas in the first charcoal tube. In this way the bulk of the neon could be delivered by operation 35. Neon was not measured accurately, but a rough estimate was usually carried out as a check against air leaks, the concentration of neon impurity in the carrier gas being known.

When argon replaced oxygen as carrier gas, it was no longer possible to burn the hydrogen in the circulating system. Therefore a large excess of hydrogen was brought in to the first charcoal tube. This may possibly have affected the adsorption properties of the charcoal for helium by competing for the vacant adsorption sites but it is not very likely. The possibility that the minute proportions of this hydrogen which would occur in fractions 12-26 would be large enough to affect the Pirani gauges was also dismissed. According to Glueckauf and Paneth (Ref. 7.2) the adsorption coefficient of of helium is 0.00117 of the adsorption coefficient of hydrogen at the temperature of liquid nitrogen. Using Glueckauf's value for the adsorption coefficient for helium and his expression for the amount of any gas in the 26 the fraction we find that the hydrogen in fraction 26 is less than 5×10^{-24} of the total hydrogen. The total hydrogen exceeded the helium by a factor of up to 10^5, but clearly the amount of hydrogen in the helium fraction was negligibly small. The amount in the neon fraction was by no means negligible, as was found empirically by the large amounts of gas appearing in this fraction, so that it was no longer possible to use the quantity of neon delivered as a check against air leaks.

In order to check the completeness of delivery of helium a calibration experiment was carried out. A known volume of pure helium was introduced into the Pirani fore-space from the calibrating system. The bulk of this was then led into the circulating system by means of the by-pass tube that ran behind the fractionating column. This by-pass was simply a ventil with very long and nearly horizontal arms, which were normally kept full of mercury but could be emptied for this purpose. (see Fig.6, Fig.8 (Q), Fig.12 (Q)). The by-pass was then closed again and the residual gas measured in the Pirani gauges. Thus the amount of helium brought into the column was accurately known. Operations 0-12 and 13-21 were performed and the amounts of helium measured. Thereafter the operations were performed two at a time and a histogram was drawn showing the amount of helium per operation against the number of the operation, (Fig.10). It was estimated that the total of helium delivered in all operations was 1.005 of that delivered in operations 12-26 so that all values for amounts of helium delivered were multiplied by this 'column factor'.

(7) The Pirani Gauges.

(a) Geheral Description. The Pirani-Hall gauge depends on the fact that the thermal conductivity of a gas at low pressures is proportional to its pressure. If a hot wire is warmed by an electric current and surrounded by a gas at low pressure, any change in the pressure of the gas increases the rate of loss of heat from the wire, cools it, and changes its resistance. The change of resistance is measured. In these measurements a modification of the Pirani gauge due to Ellett and Zabel (Ref. 7.3) was used. The walls of the Pirani gauges were kept cold by a bath of liquid nitrogen. (Liquid air was not satisfactory since its boiling point changes with preferential evaporation of nitrogen). The wires were maintained at approximately room temperature. Two identical gauges were used. One was evacuated and isolated from the rest of the system and served as a control; the gas to be measured was brought into the other gauge.. The filaments of these two gauges were in two arms of a Wheatstone Bridge circuit, in the other two arms were variable standard resistances of approximately the same order of magnitude as the resistances of the filaments (120 ohm). The galvanometer of the Wheatstone Bridge was used to measure the out-of-balance current which resulted from the change in resistance of the wire in the Pirani gauge when gas was admitted.

The gauge was not an absolute one. It was used simply for comparison and was calibrated by admitting an accurately known volume of helium from the calibrating system described in the next section. This gas came into a space consisting of the Pirani gauge itself and the so-called 'Pirani fore-space'. The volume of this space (15 ml approx.) was not known exactly but was kept the same for all measurements.

(b) Theory of the Pirani Gauges.

The following treatment is derived from Ellett and Zabel (Ref. 7.3). ~~by conduction.~~ The energy equation for an electrically heated wire in a gas at low pressure is given by:

$$E^2 / R = A k (T^4 - T_0^4) + A j p (T - T_0)$$

where E is the voltage across the wire, R its resistance, A its area, T its temperature and T_0 the temperature of the enclosure, k the product of the Stephan-Bolzmann constant and the emissivity, j a constant, and p the pressure of the gas. We neglect conduction of heat up the electric leads.

According to Ellett and Zabel, we can assume the power supplied to the wire is constant since the resistance changes are small.

Differentiating: $dT/dp = j\ (T - T_0)\ /\ 4\ kT^3 = jp$

At low pressures conduction losses are small compared to radiation losses therefore we may neglect jp in comparison with $4kT^3$.

$dT/dp = k'\ (\ T - T_0\ /\ T^3\ )$ where $k' = j/4k$.

Differentiating again with respect to T:

$d\ /\ dT\ (\ dT\ /\ dp\ ) = T^3 - 3T^2\ (T - T_0) = T^2\ (\ -2T + 3T_0)$

therefore $dT\ /\ dp$ is a maximum when $T = 3T_0\ /\ 2$.

Now let us consider the electrical equation.

The resistance of the wire is given by $R = R_0\ (\ 1 + b\ \overline{T-273})$ where R_0 is the resistance at 0°C. therefore $dR = R_0 b\ dT$

Now the change of current through the galvanometer, I_g of a Wheatstone Bridge network is $I_g = EdR\ /\ 4RR_g + 4R^2$

where dR is the change of resistance of one arm, R is the resistance of the arms (assumed approximately equal) and R_g is the resistance of the galvanometer.

Using the above results: $I_g = (k''\ R_0E\ /\ RR_g + R^2)(\ T-T_0\ /T^3\ )dp$

But since the heat loss is mostly due to radiation $E^2 = ARkT^4$ neglecting To^4 in comparison to T^4

Therefore $I_g = k'''\ \dfrac{R_0\ (AR)^{\frac{1}{2}}}{RR_g + R^2}\ \dfrac{T - T_0}{T}\ dp$

If we do not regard the power supplied to the wire as constant with changing pressure, we get the following expression for dT/dp.

$$\frac{dT}{dp} = Aj\ \frac{(T - To)}{E^2\ Rob + 4\ AkT^3 + AjP}$$

and the final expression for Ig is:

$$Ig = \frac{R_o\ (AR)^{\frac{1}{2}}\ (T - T_o)j}{4Tk^{\frac{1}{2}}\ (RRg + R^2)(R_oRbT + 4)}\ .\ dp\ .$$

Thus we see that the galvanometer deflection is proportional to the pressure change and proportional to the square root of the area of the wire, so that the sensitivity is increased by using a flat strip of metal rather than a wire with a circular cross section. As can be seen the sensitivity goes up with the temperature, but when the temperature is very high the sensitivity becomes independent of the temperature and therefore of the voltage across the wire. However it should be noted that Paneth and Urry (Ref. 7.4) using a similar apparatus found experimentally that the sensitivity curve had a maximum at about 0.5 volts and at higher voltages decreased. In order to prevent the solder from softening the temperature of the filament should not be allowed to rise much higher than room temperature. The voltage required for this was about 0.5 volts across one filament and therefore the voltage across the bridge as a whole was fixed at 1 volt and kept at this value.

(c) <u>The 'Pirani fore-space'</u>.

This is shown in Fig.11. It was the section of tubing into which helium was delivered from the column at N. The whole section was made of 4 mm tubing in order to keep the volume as small as possible. Connected to the fore-space was a compression bulb, P. The mercury in this was lowered to a point near X when helium was being delivered from the column. This exposed a volume of some 300 ml to the last charcoal tube, N, and ensured that the partial pressure of helium in the fore-space never became large enough to affect the amount delivered from the last charcoal tube. By raising the mercury until the ball-bearing T closed on its ground-glass socket the contents of the compression bulb were forced into the fore-space proper, whose limits were thus defined. R and S led to the vacuum line through which this section of the apparatus was evacuated. Z and W represent the mercury ventils which controlled entrance of helium to the Pirani gauges at V and exit to the vacuum line at O. E represents the last unit of the calibration system (described later) from which a known amount of helium was released into the fore-space.

(d) The Pirani Gauges.

These are shown diagramatically in Fig. 12a and an enlargement of the filament and its supports is shown in Fig.12b. The two gauges were mounted side by side and surrounded by a Dewar flask containing liquid nitrogen whose position is shown at K. The gauges were as nearly as possible identical. In each was a filament of flat nickel strip 0.05 cm wide and 0.002 cm thick. It was 20 cm long and mounted in the form of a W on a glass support (A, shown in side-view in right hand gauge). Tension in the strip was maintained by means of a small spring, B, which held the filament clear of the support. The ends of the filaments were soldered to hooks, C, in the tungsten leads. The tungsten was electrolytically cleaned and copper-plated before solder could be applied. This solder was an important source of weakness because it was liable to soften if the filament overheated, and was subject to attack by the mercury vapour which was always present. This led to a slackening of the wire with possible sudden changes in the radiative loss of heat and imperfect electrical contact. In consequence the gauges became occasionally very sensitive to mechanical disturbance particularly any tapping of the glass. The tungsten leads, F, passed through a pinch-seal, D, and up the inside of the tube on which the filament was mounted, E. To prevent contact one wire was sheathed in a fine glass tube, I. The leads passed out through two vacuum tight seals at the upper end, G, and were silver-soldered to copper wires. To prevent the tungsten wires from cooling in the liquid nitrogen bath, the entire inner tube was evacuated to a good vacuum and sealed at H. On one occasion a random variation in the position of the galvanometer pointer was traced to the presence of one or two cm of air pressure in this tube. The inner tube was made of Pyrex to facilitate the pinch-seal at the lower end. As the pressure of helium to which it was exposed under working conditions were extremely small indeed, no problem was introduced by the solubility of helium in Pyrex. The inaccuracy of the gauges for a few days after they had been exposed to the atmosphere may have been due to degassing of helium from the Pyrex portions. The inner tube fitted closely into the casing without touching it; the space between was part of that to which helium was admitted and was kept as small as possible. A vacuumtight seal was made with wax at the cone-and-socket at the upper end, J.

The tubes leading into (and supporting) the outer cases each contained a few grains of activated charcoal, L, resting on a glasswool plug, M. This was to adsorb any oxygen, etc. which might reach the gauges. In the tube leading to the measuring gauge there were also a few pieces of gold foil N to adsorb mercury vapour and prevent it reaching the solder. At the commencement of every day's work the gauges were immersed in hot water and evacuated for half an hour, to remove as much mercury vapour as possible. The grains of charcoal were then warmed with a small flame two or three times until a good vacuum was obtained. They were shut off from the pumps, the current through the filaments was switched on and the whole was immersed in its liquid nitrogen bath. At least five hours wererequired for temperature equilibrium to be reached.

Two mercury ventils, one of which is shown at W, controlled the flow of helium from the fore-space and to the vacuum line. The pressure in the mercury vessels was controlled by two-way taps placed near the galvanometer scale. The presence of these ventils made it practically impossible to keep the Pirani gauges free from mercury vapour and after some time actual drops of mercury appeared inside the casing of the gauges. To replace the ventils by ground-glass taps would have been advantageous.

(e) The Electrical Circuit. The circuit used is shown in Fig.13a. The two gauges, P, were in adjacent limbs of a Wheatstone Bridge. In the opposite limbs were two fixed resistances, R, of 100 ohms each and a 'Compensation apparatus', U, which transferred resistances from one limb to the other in units of 1/10 ohm. The total resistance of this was 111 ohms. The voltage (1 volt) across the bridge was provided by a 2-volt accumulator, A, placed across a potential divider, B, A rough check on the filament resistances under working conditions, (using the best values that could be found for the temperature dependance of the electrical resistance of nickel) showed that the filaments were at approximately room temperature under these conditions.

The galvanometer, G, was a mirror instrument with a sensitivity of 1450 mm / microamp at 1m and an internal resistance of 91 ohm. The scale was 1m from the galvanometer. The galvanometer sensitivity was varied by altering a large resistance in series S, and when the galvanometer was not in use it was protected by a 10,000 ohm resistance in series V, A 600 ohm resistance T across the galvanometer gave critical damping under usual working conditions.

The changes in the galvanometer off-balance current were proportional to the changes of pressure in the gauges. The deflections of the point of light on the galvanometer scale were not quite proportional to the galvanometer current because:

(i) The scale was straight.

(ii) The magnetic field in which the galvanometer coil moved was not uniform.

(iii) The elasticity of the galvanometer suspension varied with the angle of deflection.

A chart of corrections for this error was drawn up as described in the next section.

(f) Galvanometer Scale Correction.

The galvanometer was placed in position on a shock-proof support and the scale was firmly clamped in position 100 cm away. The Pirani gauges were replaced by two fixed 120 ohm resistances. A 67000 ohm resistance was placed in parallel with one of these and by switching it in and out of circuit (using a rocking mercury switch) fixed changes in the off-balance current could be produced. The scale deflections caused by the same change of current were observed in various parts of the scale. A certain arbitrary deflection was taken as standard and the excess or deficit from this per cm of deflection was plotted against the mid-point of the deflection. A table of corrections for any deflection was obtained by summing the corrections for each centimetre over which the deflection ranged. This correction was the first one applied to any reading.

(g) Measures Taken to Combat Unsteadiness.

Because the balance point of the bridge was never steady but always 'drifted' slowly, the procedure adopted for measuring a deflection took some minutes. The position of the point of light on the scale was recorded at intervals of one minute until two successive values for the rate of drift were the same to within 0.01 cm/min. The inlet ventil was then opened, a deflection occurred and readings were taken until the rate of drift was again constant. Values were extrapolated back at this rate of drift to the moment of opening the ventil, to give the point to which the pointer would have moved if the deflection had occurred instantaneously. The outlet ventil was then opened and a similar procedure was followed, the return deflection should have been the same as the previous one but in the opposite sense. If the rate of drift was large (over 0.30 cm per minute), or sudden changes in the rate of drift were occuring, considerable errors were involved. Various measures were taken to combat these two types of unsteadiness.

(i) As has already been observed, air in the inner sleeve of the gauges led to unsteadiness. This was checked from time to time.

(ii) At an early stage the electric circuit was changed from that shown in Fig.11b to that shown in Fig.11a. This ensured a more nearly constant heating effect and lowered the rate of drift.

(iii) To avoid the effects of electromagnetic induction from changing currents near-by, the leads of the Wheatstone Bridge were screened with earthed metal sheaths and the galvanometer placed in an earthed metal box. At some stages the gauges themselves were surrounded by earthed wire netting, but this device was too cumbersome. These arrangements diminished but did not eliminate the effect of certain near-by oscillators.

(iv) It was observed that a change in the light, e.g. when the rays of the sun fell on the upper end of the gauges caused unsteadiness, probably due to the heating effect.

(v) Draughts did not produce observable effects, but the tungsten-copper junctions, which were in an exposed position above the Pirani gauges, were wrapped in cotton wool to keep them from sudden temperature changes.

(vi) Mechanical shocks had a marked effect particularly when the filaments were slightly slack. Care was taken to avoid unnecessary vibrations, and particular care was exercised when raising mercury against ball-bearing float-valves in the region of the gauges.

When each of these precautions were observed, readings accurate to 0.01 cm with good agreement between 'in' and 'out' deflections were sometimes possible. Nevertheless the tendency to unsteadiness of various sorts was one serious disadvantage of this apparatus. The difficulty would have been lessened by working at lower sensitivities with greater amounts of helium. Some difficulties appeared to be inherent in the apparatus, at least in the design of apparatus used in this study; and a possible alternative is suggested at the end of this chapter.

(η) The Calibration System.

(a) **The Earlier Design.** The earlier system used provided for the taking of 5 or 6 cm pressure of pure helium over mercury and trapping small fractions of this original volume in inverted cups mounted inside the same vessel. From the volume finally remaining successive small fractions could be taken. These should give Pirani gauge deflections which would be nearly equal (decreasing slightly in geometrical progression). In fact they showed marked variations with a general tendency to increase. This led to the conclusion that helium was somehow coming into the calibration vessel, but experiments failed to show a leak and indicated that helium was coming equally into all sections. It was finally concluded that the assumption that helium was not adsorbed on the surface of the mercury, did not hold when the surface of the mercury was greasy (it had to rise through a tap greased with Apiezon grease) and when it had been exposed to pressures of 5 to 6 cm of helium.

(b) <u>The Later Design.</u> It was decided to change the calibration system for one avoiding these disadvantages. A large McLeod gauge with an accurately calibrated closed limb was used. To determine the volume of different lengths of the closed limb, the latter was filled with mercury to various heights before assembly, and the exact length of the column of mercury was measured with a travelling microscope; then the tube was weighed. The height of the meniscus was observed at the same time and the necessary correction made for its volume.

A volume of helium about 1 ml under a pressure of 2 - 4 cm of mercury could be trapped in this limb and observed through a large travelling microscope of minimum focal length 1m. With practice readings reproducible to one or two thousandths of a cm could be obtained. A hair-line mounted across the closed limb marked the upper end of the volume enclosed. Readings were taken to this mark using frontal illumination and to the shoulder of the mercury menisci in the two limbs until successive readings gave the same pressure difference. Readings were also taken to the top of the menisci using illumination from behind and a correction was made for the volume of the meniscus in the closed limb and for any pressure drop corresponding to a difference in height of the two menisci. The values for the pressure and volume of the helium sample were probably accurate to two parts per thousand.

This sample was expanded into the volume of the whole McLeod gauge plus the spaces marked B and C in Fig.14. The space C whose volume was known extended from the mercury cut-off at the right to the mark on the tube to the left, which was level with the cut-off and to which mercury was raised. When C was isolated by raising a column of mercury to the cut-off a known fraction of the original volume was enclosed. This was then allowed to expand into spaces D and E. A known fraction was isolated in E and could be introduced into the Pirani fore-space by lowering the fourth mercury ventil to a fixed mark M. Space E was then part of the Pirani fore-space. Similarly the second ventil was always adjusted to a mark N which defined D. If a smaller amount was required, as was usually the case, the fraction trapped in E could be allowed to expand back into space D and C after they had been carefully evacuated for about an hour.

The volume of the whole McLeod gauge was determined by filling it with water from a 100 ml burette, which was afterwards calibrated at the same temperature by weighing 100 ml portions of distilled water. The volumes B, C and E were determined by filling them with triply distilled mercury at 21^{o}C. and weighing them carefully before assembling. The junction between B and the McLeod gauge was made carefully so that no volume change was involved. The space D was calibrated as follows after the system was assembled. An amount of helium was taken and measured in the McLeod gauge. A proportion of this was isolated in spaces C, D and E and the McLeod gauge was evacuated. The helium remaining was then allowed to expand into the whole and the pressure was again measured in the McLeod gauge. The ratio of the first value of the pressure to the second was as A+B+C+D+E to C+D+E. The mean of four values was taken and the volume of D calculated. The volumes were:

A (McLeod)	536. 0 ml
B	4.15 ml
C	4.207 ml
D	162.3 ml
E	4.663 ml

Errors.

We may allow an error of 0.25 ml in the calibration of the McLeod gauge volume and 0.1 ml in setting the mercury to the mark at the base of the gauge, a total error of 0.07%. The error in the volume of B was negligible compared to the volume already allowed in A. The errors in the calibration of C and E were unlikely to amount to more than a cu.mm or 0.025%. If the error of setting the mercury to the various marks was as much as 1/10 mm there was a resulting uncertainty in the volumes of C and E of about 4 cu.mm (in 7 mm tubing) or 0.1%. The error in the four readings giving the value for D was less than 1 in 1000 and the error of setting mercury was only that at N plus that at the cut-off between C and B. The former was 4 cu mm, the latter 80 cu. mm because the mercury had to be raised 2 mm over the edge of the cut-off to make certain that no helium leaked past. The error in D was therefore 0.025%. The total error in the calibration system may therefore be 0.3%.

The expression for the sensitivity of the Pirani gauges to helium in terms of cm deflection of the galvanometer pointer per ml of helium at N.T.P. is as follows: (in the case where helium is 'back-expanded')

$$\underline{\text{Sensitivity}} = \frac{\text{Deflection}}{\text{Volume of helium}} \times \frac{76.00}{\text{Press}} \times \frac{273.2 + t}{273.2} \times \frac{A + B + C}{C} \times \frac{(C + D + E)^{2}}{E^{2}}$$

$$= \frac{\text{Deflection}}{\text{Volume}} \times \frac{273.2 + t}{\text{Pressure}} \times \underline{4.85} \times 10^{5} \quad \text{cm/ml}$$

where t is the Centigrade temperature.

A factor had to be applied to all calibration readings except the first to allow for the fact that there was less helium in space D every time a sample is removed. This factor is given by:

$$\frac{C + D + E}{C + D} = 1 + \frac{4.66}{166.5} = 1.028$$

For the nth successive calibration reading the factor was $(1.028)^{n-1}$

The sensitivity of the Pirani gauges varied from day to day by amounts up to 10%. Therefore they had to be recalibrated for every determination. Fresh helium was always taken in the calibration system. In case there was a gradual change of sensitivity during the day, two samples were admitted to the gauges before the reading was made on the unknown sample of helium and two readings immediately after.

(e) The Carrier Gas System.

The system containing the gas for flushing helium and radon out of the radium flask is shown in Fig.15. It consisted of a ten litre vacuum-tight steel flask, A, and smaller glass flasks, B, totalling 1.5 litres in volume. These large flasks were necessary because considerable volumes of gas were required. In most of the work here described oxygen was used as the carrier gas but at a very late stage argon was used instead. The gas used in previous work was a mixture of hydrogen and oxygen prepared by electrolysing a strong solution of caustic soda in a cell attached to the radium flask. This system had the advantage of flexibility but extra oxygen had to be introduced to burn the hydrogen quantitatively and there was always the danger of a small explosion. It would have been convenient to have used electrolytic gas for the long flushing out of radon, thus decreasing the volume of carrier gas to be stored, and to have used oxygen or argon for flushing helium into the circulating system.

The oxygen used was of ordinary cylinder purity. It was led in at C in Fig.15, past the inlet tap E and allowed to bubble away to the air in a small jar of mercury, D. This ensured that there was always a pressure greater than atmospheric in the rubber tubing and prevented contamination with air. The inlet tap was then cautiously opened, admitting the oxygen; usually the oxygen was not admitted to the 10 litre flask immediately but was purified from helium first. When the glass flasks were full to atmospheric pressure as indicated by the manometer K, the oxygen was condensed in the cold finger, G, cooled in liquid nitrogen. When the cold finger was full of liquid oxygen (15 - 20 ml, enough to give 10 litres of gas) enough to fill the glass vessels to atmospheric pressure was allowed to evaporate. Most of the helium or neon would evaporate also. The tap L was then shut and the oxygen adsorbed at liquid nitrogen temperatures on the charcoal (50 gm) contained in tube F. When the pressure had fallen to less than 1 mm, the tap H, to the vacuum pumps was opened and the residual gases which would contain a larger proportion of helium and neon were pumped away for a period of 20 min. The oxygen was recondensed in the cold finger and the procedure was repeated eight or nine times until all the helium had been removed.

It was then desirable to remove at least some of the nitrogen which might have been present as quite a considerable impurity. The gases contained in the storage vessels at any time when the tap L was open amounted to 15 cm pressure of oxygen together with the bulk of any nitrogen. The tap L was shut and the whole of this vapour was pumped away. Finally all the condensed oxygen was slowly evaporated, the ten-litre flask being opened to accommodate it. To determine the concentration of helium remaining as impurity a blank experiment was always carried out with a normal quantity of oxygen. The upper limit was regarded as 3×10^{-9} ml helium. (i.e. about .01 - .05 of the usual amount of helium produced from the radium). The volume of oxygen taken was always estimated by the pressure it produced in the circulating system, and making a correction, the uncertainty in the result due to contaminating helium in the carrier gas was reduced to negligible proportions.

When it was no longer possible to use oxygen (Chapter Vl, section γ) and argon replaced it, the same procedure was used. Argon was selected because its physical properties were similar to those of oxygen. Nitrogen could not have been condensed in the cold finger. To remove oxygen, cylinder argon was passed over heated copper turnings before use. These were contained in a silica tube about 60 cm long maintained at a low red heat. Ten litres of argon were passed slowly in 40 min. The steps taken to remove helium were the same as those described above.

(ι) Experiments with Air Samples.

The helium content of air is an accurately known geophysical constant (Ref. 7.5). Therefore by taking a known small volume of air free from water and carbon dioxide and measuring the helium in it, a useful check on the accuracy of the measuring apparatus could be obtained. An air pipette was made consisting of a short length of capillary tubing (volume 0.1 ml) enclosed by vacuum-tight capillary taps. Five experiments gave values for the concentration of helium in (CO_2 - free) air as

$$\left.\begin{array}{l} 5.22 \times 10^{-6} \\ 5.14 \times 10^{-6} \\ 5.21 \times 10^{-6} \\ 5.27 \times 10^{-6} \\ 5.29 \times 10^{-6} \end{array}\right\} \quad \begin{array}{l} \text{Average} = (5.23 \pm .06) \times 10^{-6} \\ \text{The best experimental value is} \\ \qquad\qquad 5.25 \times 10^{-6} \end{array}$$

This margin of error (0.12%) arises from uncertainty and lack of good agreement in readings on the galvanometer scale and is largely due to unsteadiness of the Pirani gauges. Nevertheless it was possible to commence work with a solution of radium salt.

(κ) Conclusions Concerning the Helium Apparatus.

The apparatus used was not subject to any major alteration during the experiment, except that to the calibration system which has been described. As a result of this work, it is concluded that the apparatus measures helium with accuracy, although certain improvements can be suggested.

(i) The glass in some sections of the apparatus used was old and gave reason to believe that it had been subject to a certain amount of devitrification. Any future work should be carried out on a newer apparatus.

(ii) In the carrier gas system it is suggested that electrolytic gas, continually generated at a rate which could be exactly controlled, be used for the eight-hour period of radon removal, and oxygen for the sweeping out of helium only.

(iii) The type of flask used for direct freezing experiments should be Type 1 (see Fig.4) in preliminary work, because the flask is then more easily altered; but type 11 should be used for accurate measurements because there is then less risk of solution being splashed onto a ground-glass joint.

(iv) The flow of carrier gas should be controlled by a more sensitive valve.

(v) Pressure on the outlet side of the flask should be kept at 5 cm of mercury at least; this requires some sort of mercury bubbler more elaborate than the simple one used in this experiment, which could only regulate a pressure drop of 2 - 3 cm. Similarly the ventil leading from the radium system into the circulating system should be adapted to deal with a 5 cm pressure drop.

(vi) The column by-pass should have a ground-glass tap in either limb, or alternatively, a very-well-fitting float valve at the upper end of each limb. It would then be possible to allow air at atmospheric pressure into sections of the apparatus without having to allow air into the whole.

(vii) The working of the fractionating column could with advantage be made automatic.

(viii) The flow of gas into and out of the Pirani gauges should be controlled with taps and not with mercury ventils, and the gauges should be protected in every possible way from mercury vapour.

(ix) If this is done, and great care is taken to avoid overheating the filament it should be possible to use the Pirani gauges for a year or more without rewiring. In that case a design can be suggested which may reach temperature equilibrium more quickly than does the type described in this chapter. The inner sleeve and the outer casing should be joined by a ring-seal just above the filament, which would reduce the volume of the gas space to which helium is admitted. There would then be only one thickness of glass between the liquid nitrogen and the tungsten leads, evacuated inside as before. There would be no ground-glass cone and socket in the main tube above the level of the liquid nitrogen, but there should be a Pyrex to soda cone-and-socket connection in the side arm. The level of liquid nitrogen could then be brought to a point very near the top of the evacuated space. These alterations should speed the rate of attaining temperature equilibrium and cut down the rate of drift of the balance point.

(x) The wires of the Wheatstone Bridge circuit should be screened and, ideally, so should the Pirani gauges themselves. There is not a great decrease in stability when the latter precaution is neglected.

(xi) In the calibration system, there was a rather large error involved in setting mercury to various marks. This could be minimized by making the tubes narrower at these points or by arranging for an automatic controlling device. An electrical contact sealed into the wall of the tube at the right point is one possibility, provided there was no arcing which might drive occluded hydrogen out of the walls.

(xii) A cathetometer with a much shorter focal length than the one used is highly desirable for measuring the helium in the McLeod gauge.

(xiii) Many of the errors would be reduced by measuring a larger quantity of helium, say 10^{-6} ml.

CHAPTER V111

RESULTS AND DISCUSSION.

(α) Corrections Applied.

(β) Results.

(γ) Possible Sources of Error.

(δ) Conclusions and Suggestions.

(α) Corrections Applied.

The following corrections were applied to the results:

(i) Correction for non-linearity of Scale (Chapter V11 Section ζ)

(ii) Correction to calibration readings for successive calibrations (Chapter V11 Section η).

(iii) Correction for Incomplete Delivery of Helium from the Column (Chapter V11 Section ε).

(iv) Correction for Helium in the Argon. A control experiment carried out after the third final measurement showed a proportion of helium in the argon to the extent of 3.0×10^{-9} ml of helium for every cm of argon pressure in the circulating system. (It will be remembered that the quantity of carrier gas was estimated by the pressure it produced in the circulating system). A later experiment showed 3.5×10^{-9}ml per cm pressure. This was consistent with the supposition that a slight air leak had developed in the argon storage system. By taking as zero time the last occasion on which the carrier argon had been purified a correction for this error was made.

(v) Due to one or other of the causes discussed in Chapter Vl, Section γ, a progressively increasing proportion of radon was found retained in the radium flask after each eight-hour period of removal. The proportion retained was estimated by means of a portable dose-meter, using a sheet of lead to reduce the effects of all radiation but the gamma activity due to radium C. A residual activity of 1.5% was found after the fourth measurement and 1.7% a few days later. The assumption was made, supported by these figures, that this error had grown regularly with time since the introduction of the radium solution, and a value for the residual activity was obtained for each measurement. Then the Bateman factors were corrected according to the formula $\beta' = 4x + \beta(1 - x) = \beta + (4 - \beta)x$.

Before the fourth measurement recorded below fresh supplies of argon were taken. During the flushing out of helium for this fourth measurement the tip of the bubbler in the radium vessel blocked partially. It is just possible that flushing out of helium was incomplete. This would make the fourth result too low, but since it is already higher than the others, the effect cannot have been great.

(β) Results.

The results of the four measurements made are tabulated below. It will be seen that agreement betweem them is poor . In the first column is the observed deflection in cm. In the second column is the volume of helium corrected for the argon blank and the column factor. In the third column is the time of accumulation of helium. In the fourth column the product of this time and the Bateman factor (corrected for ratained radon). Finally is the rate of helium production due to radium alone in ml per hour. The figures in the final column should agree.

TABLE V.

RESULTS.

No.	Deflection.	Volume(at NTP)	t	t β'	Vol/hour.
1	8.63 cm	4.02×10^{-7} ml	85.7 hr	150.5hr	2.68×10^{-9}ml
2	7.60 cm	2.05×10^{-7} ml	47.33hr	70.3hr	2.92×10^{-9}ml
3.	7.25 cm	1.93×10^{-7} ml	45.0 hr	66.3hr	2.91×10^{-9}ml
4	17.95 cm	5.22×10^{-7} ml	90.43hr	167.4hr	3.12×10^{-9}ml

(NB. The scale sensitivity for the first reading was smaller than for subsequent readings).

The average value for the rate of helium production is:

$$(2.90 \pm 0.15) \times 10^{-9} \text{ ml per hr}$$

$$= \frac{2.88 \times 6.023 \times 10^{23} \times 10^{-9}}{22400 \times 36000} = 2.18 \times 10^{6} \text{ disintegrations per sec.}$$

The standard deviation of the four results is 5.1%.

As has already been mentioned no estimate of the mass of radium in the solution was made, partly because of the wide discrepancy in these results and partly because of the difficulty experienced in recovering the radium from the flask.

(γ) Possible Sources of Error.

The results of the four measurements do not vary systematically with either the period of accumulation or the quantity of helium taken for calibration. The first measurement and the fourth are the ones with the longer period of accumulation of helium. One would expect them to be either both higher or both lower than the other two, yet the first gives a lower result and the fourth a higher. Similarly these are the two measurements where the largest volume of helium was taken for calibration purposes. Even if we discard one of these two readings as incorrect for some other reason, the close agreement between the second and the third readings, where widely different amounts of calibration helium were taken, argues against systematic errors in the calibration system.

The only regularity which can be observed is a rise in the values obtained during the time of the experiment. This could not be due to adsorption or desorption of helium by the varnish and no signs of any leakage of atmospheric helium could be detected. Correction has already been applied for helium in the argon.

One likely possibility arises from the surface effect whereby alpha particles arising from a point in the solution near the walls may come to rest in the walls and so be lost. The effect is increased because of the 'emulsifying' tendency noticed where solution and mercury met, and also perhaps because of a hypothetical absorption of radioactive substances on the mercury or the varnish. The figures require that this effect should be greatest at the start of the readings.

The second possibility is progressively increasing retention of radon. This could be easily explained in terms of an unobserved breakdown of the varnish causing precipitation of silicate, or of absorption of radon on the varnish etc. Correction has already been made for this possibility and to invoke it to explain the results would be to cast doubt on the activity measurements which were the basis of the correction. There is no single simple explanation, therefore, of the variation in the results of the four determinations.

(d) Conclusions and Suggestions.

Work has been carried out on the problem of determining the half-life of radium by measurement of the helium evolved. The apparatus and technique of Glueckauf as modified by workers at the Londonderry Laboratory for Radiochemistry was used to measure the quantities of helium. Various solutions of radium and various methods of extracting the helium from solution has been investigated. In order that a quantitative result be obtained if possible, the most promising short-term approach was followed, and measurements were carried out on the rate of evolution of helium from a radium solution. The wide scatter of these results and the difficulty experienced in recovering the radium at the end of the series of experiments did not warrant the making of an accurate analysis of the weight of radium present in the flask with the result that no value for the half-life of radium can be given.

The method finally used involved floating the radium solution on a layer of mercury whose level could be adjusted to minimise the gas-volume above the solution. The advantage of this type of apparatus was that it avoided the necessity of freezing the solution. This in turn permitted the use of a coat of varnish to protect the glass of the flask from attack, so that soda-glass which is impermeable to helium might be used for the flask. The difficulties in the use of such a flask have been set out in Chapter Vl, section δ and will be summarized here.

(i) Radium and/or its daughter products appeared to have been absorbed on the surface of the varnish or the mercury.

(ii) Solution tended to be trapped between the mercury and the walls of the flask when the mercury was raised.

(iii) The presence of a greased vacuum tap in a position where solution is likely to be splashed upon it and through which solution had to be introduced or removed was a disadvantage. For these reasons the floating-on-mercury type of flask is not recommended.

The alternatives are set out in Chapter V1 Section δ. They include the use of a soda glass flask with a sulphuric acid solution, a plastic flask with an aqueous solution and a mild cooling agent, a chemically resistant metal flask with an aqueous solution, a Pyrex flask with a jacket of soda glass and a low freezing liquid in between, and a radium amalgam.

Various minor changes to the helium apparatus have been suggested in Chapter V11, section (k). The question may arise whether the bulky and sometimes cumbersome helium apparatus is all necessary for the measurement of helium. The heart of the apparatus is the fractionating column whose shape is dictated by the method of fractionation which must remain unchanged. It can be reduced in size and a smaller version is in fact in use at Durham. For measuring the purified helium there are various alternatives to the Pirani gauge, the most interesting of which is the ionization gauge, recently much improved by Alpert and Buritz (Ref.8.1). This instrument is capable of measuring very small pressure changes (of the order of 10^{-10} mm) so that it would probably be possible to use it to record continuously the changes of pressure as helium was delivered from the column into a space of some 100 ml. A calibration system would still be required, and for this a McLeod gauge and pipetting system are most straight-forward.

The only part of the apparatus that might be dispensed with is the circulating system; the gases would then be led through a non-return valve from the radium flask directly into the first charcoal tube of the column. Hydrogen would then be separated on the column. If the apparatus were to be used also for other problems, however, burning of hydrogen would be necessary. All the other parts of the apparatus are essential and form an accurate and reliable instrument which probably affords the only way of analysing such small quantities of helium as are produced in radium solutions.

A final summary and conclusion for this work is not easy because there is no numerical result. The conclusions therefore must take the form of the suggestions for future work which have been given. In deciding the question of whether or not further work on this determination of the half-life of radium is warranted, such other factors as the availability of a standard source of radium and a measuring apparatus must be considered. The construction of a new helium apparatus would not be worth while unless it were required for other purposes as well. If a measuring apparatus and a standard source of radium are available then the work is well worth continuing, because the advantages of the helium method (outlined in Chapter 11,Section δ) still remain. The difficulties are many, to overcome them will take some time, yet they are not insuperable and it is hoped that the present work will aid the determining of a new and more reliable value for the half-life of radium.

It may be asked how the helium method compares with other methods that have been used for determining the specific activity of radium. In view of the difficulties encountered in this work it may well be questioned whether the helium method lives up to the advantages which it is supposed to have and which have been stated in Chapter 11, Section (δ). But as no method can be ruled out as long as the difficulties involved are technical ones and not difficulties of principle. No doubt technical difficulties were encountered in all the experiments described in Chapter 11, these cannot be estimated by reading the papers in which the work is described. The helium method, then, as far as the principle goes, is still among the best.

Sometimes, however, the technical difficulties reach a stage at which the method, if not abandoned, must be set aside until new techniques or new materials are developed. The helium method has not quite reached this stage yet, but if the various not-very-promising possibilities which have been suggested should prove impracticable, then this stage will have been reached.

Of the other methods, the growth-in-ionium method suffers from a disadvantage of principle, the uncertain geological history of the minerals used.

The direct-counting method reaches its most advanced form yet in the work of Kohman. However the numerous corrections which have to be made to allow for loss of radon from the source amount to a difficulty of principle. This difficulty covers all methods using sources containing radium itself. On the other hand, to use a Ra(B + C + C') source involves a gamma standardization under conditions where the absorptions of containers, etc. cannot be accurately allowed for. This again is a difficulty, not of technique, but of principle. Of all the methods involving direct counting, that of Ward, Cave, and Wynne-Williams appears to be the best.

Mann's experiment is clearly the best of those based on heating effect. Here is one case where further advance must await refinements in related fields, namely a more accurate determination of the degree to which the beta and gamma radiations of the decay series are adsorbed in thin-walled vessels. When this is available Mann's instrument will probably provide a better method than the volumetric measurement of helium.

The method of measuring the rate of transfer of electric charge as used by Braddick and Cave is probably equal in reliability to Ward, Cave and Wynne-Williams' work and may perhaps be regarded as equal to, but not superior to, the helium method.

All the work described in this thesis was carried out in the Radiochemistry Laboratory of the Durham Colleges in the University of Durham. I should like to thank the Council of the Durham Colleges for the Research Assistantship that made the work possible. I should also like to express my thanks to Prof. F.A. Paneth for suggesting the problem and his helpful advice; to Mr. G.R. Martin for invaluable help and criticism; to Dr. P. Reasbeck for instructing me in the techniques of the helium apparatus, and to many other people in the Radiochemistry Laboratory for practical help and advice.

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PLATE I The Carrier Gas System, The Vacuum Pumps, and the Radium Flask

Mercury Vapour Pumps (behind screen)

High Vacuum Line

Secondary Vacuum Line

Secondary Vacuum Control Tap

Rotary Oil Pumps

Carrier Gas System

Control McLeod Gauge

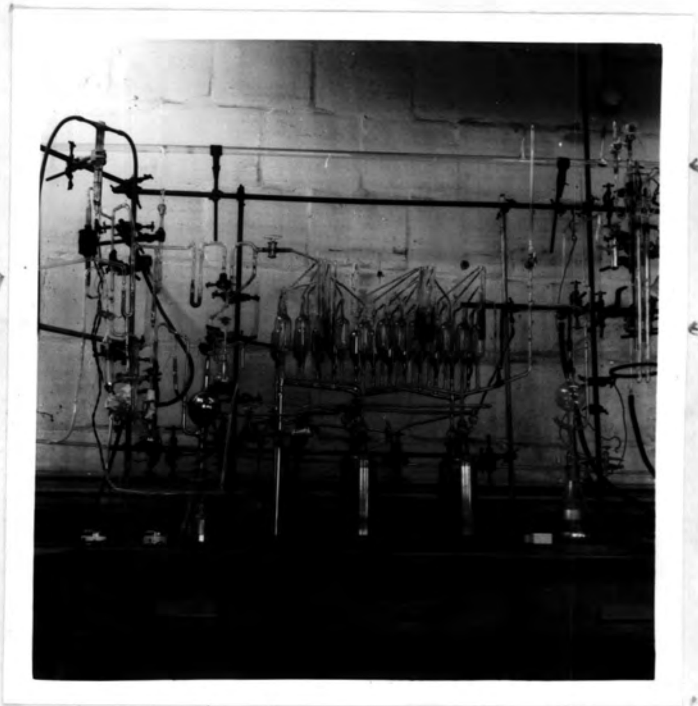
Radium Flask

Position of Radon Traps

Radon Guard Tube

Circulating System

PLATE II The Fractionating Column, the Circulating System, and the Pirani Gauges



Tube leading from radon traps

High Vacuum Line

Pirani Ventils

Charcoal tubes of Fractionating Column

Circulating System

Fractionating Column

Pirani Gauges

Toepler Pump

Compression Bulb in Pirani Fore-space

PLATE III Pirani Gauges and Calibrating System