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MICRO-GAS ANALYSIS IN RELATION TO RADIOCHEMICAL PROBLEMS.

—— THESIS ——

presented in canditature for the degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF DURHAM.

by

EDWARD JAMES WILSON, B.Sc.

DURHAM COLLEGES ★ UNIVERSITY OF DURHAM
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The work described in this thesis was carried out in the Radiochemical Department of the Science Laboratories, Durham, between September 1947 and August 1949 under the supervision of K. F. CHACKETT, B.Sc., Ph.D.

ACKNOWLEDGEMENTS.

I wish to take this opportunity of thanking Dr. K.F. Chackett for his expert guidance and the enduring patience with which he has supervised my work during the past two years. I heartily thank Professor Paneth for suggesting the problems tackled, for his perpetual interest in the work involved and for all his very useful advice and encouragement.

Appreciations are extended to the Keeper of the Minerals in the British Museum (Natural History) for the liberal supply of meteorite samples, and to the personnel of the University of Michigan and the U,S. Signal Corps. concerned with the V2 flights, for the stratosphere air samples.

My thanks are also due to the Department of Scientific and Industrial Research for the grant covering the full two years.

SUMMARY.

The thesis comprises four entirely separate problems, but each involves the determination of minute quantities of helium.

Earlier work in the field of helium measurement is reviewed, special emphasis being laid on the work of the two investigators, Lord Rayleigh and Professor Paneth. A full description of modern Helium technique is given.

The first experiment was concerned with the disintegration constant of Uranium I. The micro-chemical method of determination had been carried out by Gunther, who obtained a somewhat different result from the value calculated by physical methods. Following Gunther's procedure, we used uranium nitrate solutions, but accomplishing the experiment within three weeks as compared with his three years, we were able to show that the value of the disintegration constant, calculated from the volume of helium produced, was in fair agreement with the physical value. As the other experiments seemed more urgent, the uranium experiment had to be abandoned with only three results obtained.

Stratosphere air samples collected by V2 rockets in America were analysed and the composition of the gases nitrogen, argon, neon and helium estimated. Oxygen was removed by a heated copper spiral, and the helium and neon separated by fractional adsorption on charcoal and measured separately with Pirani gauges. Argon was determined by a McLeod gauge after removal of nitrogen in a Calcium furnace. The composition of the stratosphere at 50 km. and 70 km. is practically the same as ground air, which constitutes evidence

that turbulence still overcomes diffusive segregation up to that altitude.

Bauer's theory that cosmic radiation produces helium in meteorites was disproved in our third experiment. Samples of meteorite taken from the centre and the outer edge were shown to have the same helium content; if cosmic radiation had resulted in the production of helium, there would be an appreciable excess in the edge samples, due to the absorption of cosmic rays by the material of the meteorite. We were surprised to find how homogeneously distributed the radioactive elements must be on the whole mass of one particular meteorite.

In conjunction with other work being carried out in the department, the helium content of certain Beryls and Magnetites were determined. Heating of beryl crystals with caustic potash at a temperature of 700°C for one hour released all helium from the beryls, but it was necessary to use powdered magnetite heated with fusion mixture at the same temperature for 3 hours to perform the same function. The values found agreed with those of Lord Rayleigh.

CONTENTS.

Chapter 1. Historical Introduction.

Page No

Chapter 2. The Helium Apparatus.

Chapter 3. Re-determination of the Disintegration Constant of Uranium.

Page No

Chapter 4. Chemical Composition of the Atmosphere.

Chapter 5. The Measurement of Helium in Meteorites.

Chapter 6. The Helium in Beryls and Magnetites.

— CHAPTER 1 —

CHAPTER I.

HISTORICAL INTRODUCTION.

1. THE HELIUM WORK OF LORD RAYLEIGH.

The identification of the inert gas helium as a constituent of the sun was first recorded by Lockyer in 1868 (L,2,L3). It was not until 1895, however, that the existence of the gas in terrestrial minerals was detected by Ramsay and Crookes by means of its characteristic spectrum (R1). Even then, before radioactivity had been discovered by Becquerel, Ramsay had noticed the peculiar association of the gas with minerals of uranium and thorium. In 1902, Rutherford and Soddy explained the phenomenon by the production of doubly charged helium nuclei ejected from disintegrating atoms of radioactive elements, subsequently collecting two electrons from the matter of the mineral or rock and becoming a neutral atom.

Since this discovery a great deal of important work has been accomplished by Strutt (the late Lord Rayleigh) in the measurement of the gas, and comparison of the volume with the quantity of the radioactive material present. His experiments commenced in 1908, in which year he showed that practically all rocks contain a certain proportion of helium, and that there was only one case where the helium content was far in excess of that which could be explained by the presence of uranium and thorium. This outstanding case was the mineral Beryl - even today there is no explanation for this excess (S.1,S2). Strutt used large quantities of rocks and minerals, sometimes as much as one kilogramme, and partially released the helium by heating the minerals to redness for two hours. He estimated that at least 50 per cent of the occluded gas would be released in this manner. Nitrogen, the main constituent with helium and argon, was removed by sparking it with an excess

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of oxygen, and charcoal cooled to -80°C was employed to purify the helium from all other gases. The actual volume was measured in a McLeod Gauge capable of detecting quantities as small as 10^{-6} cc. gas (S3,S4).

Lord Rayleigh did not tackle the subject again until 1933 when he again attempted to explain the presence of excess helium in beryls. By heating beryls from known geological formations he was able to show that the large helium content was limited to specimens of great geological age, and never found in younger specimens. He concluded that the helium must come from some other element besides uranium or thorium. (R2).

2. THE HELIUM WORK OF PROFESSOR PANETH AND HIS COLLABORATORS.

Practically twenty years elapsed after the initial work by Lord Rayleigh before any further interest was taken in the presence of helium in rocks, when it was realised that important information could be gleaned by determining the ages of various types of rocks and meteorites, the quantities of radioactive elements being so small that other age methods were unsuitable.

In 1928, Paneth and his collaborators had constructed apparatus, which employing spectroscopic detection, was capable of detecting with certainty quantities of helium and neon down to 10^{-10} cc. By this means they could even detect 10^{-5}cc. of air by the presence of neon lines alone. (P9.)

They utilised the apparatus to test the possibility of the formation of helium artificially from other elements, under various conditions such as bombardment of potassium salts by cathode rays, passage of an electric discharge through hydrogen or compounds of hydrogen, and action of α and β rays on water and mercury. With the necessary precautions taken to exclude the entry of air or diffusion of helium from air through hot glass, they were able to show that no helium in quantity larger than 10^{-10} cc. was obtainable by these methods (P10).

The third experiment carried out proved that glass is permeable to helium at the ordinary temperatures and that at 0.5 atmosphere pressure about 10^{-16} cc/cm^2/hr. passes through soda glass of thickness 0.5 mm. Since the rate of diffusion of neon under the same conditions is practically negligible, neon-free helium can be obtained with little difficulty (P10).

The measurement of helium in various gas wells of Germany was accomplished later that year. The helium and neon were purified by the removal of oxygen, nitrogen and carbohydrates with heated calcium. Further purification with cooled charcoal removed argon, and the ratio of helium to neon was determined spectroscopically after first measuring the volume. Most gas wells were shown to contain only about 0.006 per cent helium compared to the 1 per cent or more in American wells (P4).

In the same year a new research was begun on the determination of the age of meteorites using the Helium Method. The minute quantities of gas were removed from small portions of iron meteorites by dissolving them in complete absence of air. Quantities of helium varied between wide limits e.g. 2×10^{-10} cc. to 2×10^{-5} cc. per gram. (P5).

The determination of the helium content of "moldavites" and artificial glass comprised the sixth experiment. The rare gasses were released when the moldavites were heated or fused with sodium carbonate, and the ratio of helium to nitrogen plus argon was greater than the corresponding ratio in the atmosphere. It was shown that the excess helium was in the region of 1.6×10^{-5} cc. per gram of material. This excess helium was due to the glassy nature of the moldavites, since artificial glasses have the power of concentrating helium greatly in comparison with neon. In fact, at a little below atmospheric pressure, they dissolve in equal times at the ordinary temperatures, approximately ten times as much helium as neon. In spite of the very small partial pressure of helium in the atmosphere, this action is sufficient to explain the greater part of the helium content of moldavites, since artificial glasses in which the helium cannot be of radioactive origin but must be derived from air, has a helium content amounting to 4.2×10^{-6} cc./gm. Determination of the age of moldavites and other types of glassy materials by the helium method is therefore impossible (P11).

In 1930, a hot wire manometer - Pirani Gauge - was first employed to measure the minute quantities of helium and neon. The gauge and a compensating manometer occupied two arms of a Wheatstone Bridge. The galvanometer deflection was shown to bear a linear relationship both to the total pressure and to the percentage of helium in the mixture. Quantities of helium from 7×10^{-9} cc. to 1×10^{-4} cc. could be determined with an error which falls from 50 to 1 per cent within the limits stated (P12,P13).

Later the following year an improved apparatus was developed which was capable of dissolving materials in acid without the admission of air or of radioactive impurities. By employing this in conjunction with the hot wire manometer, the helium of the iron part of the meteorites was determined. In 38 meteorites, the values lay between 0.23 and 36×10^{-6} cc/gm. The non-ferrous parts appeared to contain only slightly smaller quantities. Investigation of the liberation of helium from ferrous meteorites was undertaken, and shown that on heating to 1000°C for several hours, only about 2 to 6 per cent of the total helium was liberated (P13).

Helium Researches X described a method which permitted the determination of radium emanation of the order of 10^{-13} curies with an error of about 20 per cent. In combination with the helium method, the ages of meteorites were calculated (P8.).

In 1935, Gunther and Paneth were able to detect as little as 0.1 per cent hydrogen and 0.002 per cent neon in 10^{-7} cc. helium. They were able to show that the air near the ground contained less than 2×10^{-4} per cent hydrogen. (G6.)

In 1935, Professor Paneth worked in conjunction with Professor Holmes to determine the ages of the inclusions found in kimberlite, the minerals from the diamond pipes of South Africa, using the helium method. Specimens of rocks were heated with various fluxes at various temperatures to estimate the correct conditions for complete liberation of helium. Heating to a temperature of 800°C to 900°C for two hours proved the simplest method of driving out all the helium. The helium ratio of kimberlite corresponding to an age of 58 million years was consistent with the late Cretaceous Age assigned to the diamond pipes (H2).

In the same year, experiments were carried out on the spectroscopic identification and manometric measurement of artificially produced helium. Neutrons from 2.04 curies of radon mixed with beryllium, produced during its decay 2.4×10^{-7} cc. helium by the reaction :-

$$ {}^{10}_{5}B + {}^{1}_{0}n = {}^{4}_{2}He + {}^{7}_{3}Li $$

(P7).

More work on artificially produced helium was accomplished, during 1938, when attempts were resumed to explain the large excess of helium in beryls. The work entailed the identification and measurement of helium produced by the action of γ-rays on beryllium. It was concluded that the disintegration product of beryllium, which emits neutrons when irradiated by γ-rays, is two atoms of helium and not the isotope of beryllium of mass 8 (G2).

+In Helium Researches XV, various specimens of old beryllium metal were analysed for helium; the experimenters not finding any, concluded that the helium of beryl could not be ascribed to disintegration of ^{8}Be, nor to the influence of natural sources of γ-rays. Since beryllium itself does not produce adequate amounts of helium, the helium in beryls must be ascribed to some other element (F1).

Prior to 1946, micro analyses of the helium and neon contents of atmospheric air had been carried out by Glueckauf in Professor Paneth's laboratory. He had constructed a fractionating column so that helium and neon could be fractionally adsorbed on charcoal, subsequently separated and measured individually with a Pirani gauge. Atmospheric air at ground level was universally of the same composition, but there were indications of a slight increase of helium in the stratophere above 20 km. although the figures were not conclusive. (G3).

3. OTHER WORKERS IN THE HELIUM FIELD.

When, after Rayleigh's pioneer work, the helium method of age determinations fell into disrepute, investigators did not appreciate the fact that radioactive rocks may retain the bulk of the helium despite the high pressures set up within them during geologic time. Lack of sensitive apparatus made it impossible for them to measure the helium content of igneous rocks where the concentration was only about one millionth of that found in radioactive minerals.

Dubey working in Professor Holmes' and in Professor Paneth's laboratories (D1), made the first helium age determinations of igneous rooks when he measured the radium, uranium, thorium and helium in rocks from the Whin Sill and Cleveland Dykes, and estimated the respective ages to be 182 million years and 26 millions years. Naturally these ages are a minimum.

Between 1932 and 1936, an elaborate time scale was evolved largely through the work of W.D. Urry (U1). It was most convincing that the ages obtained were in apparent agreement with those obtained by the lead method.

In 1936, Evans and his co-workers began their researches into the subject, and because of the apparent success of the method, they constructed apparatus which was capable of "mass production" of age results (E2).

The method involved the use of a direct fusion furnace first used by Evans in 1935 (E1), but modified so as to be more airtight. Fusion was carried out between 1500°C and 2000°C when 99 per cent helium was released within 5 minutes. Hydrogen from the gases evolved was removed by passing over cupric oxide heated in the presence of pure oxygen. The normal charcoal tubes were employed for adsorption of all gases except helium, and measurement of the latter was accomplished with a McLeod Gauge. Results were accurate to 2 per cent for 10^{-4} cc. helium.

Evans and Goodman concluded that although other methods of age determinations had been discovered, the lead and helium methods still remain the outstandingly promising radioactive ones.

— CHAPTER 2 —

CHAPTER 2.

THE HELIUM APPARATUS.

1. PRODUCTION OF OXYGEN.

Air free, and consequently helium free oxygen, is necessary as a flushing agent, and for the removal of hydrogen. Originally the gas was prepared by electrolysis of caustic soda using nickel electrodes, the hydrogen and oxygen evolved being stored in separate reservoirs. The present arrangement, suggested initially by Glueckauf, involves the preparation of oxygen alone by the catalytic decomposition of hydrogen peroxide by platinum black. Providing the piece of platinum black is large enough (about 12 cm^2) and freshly prepared, the reaction can be extremely rapid, at least two litres NTP of the gas being prepared within an hour.

The main oxygen line and storage bulb (Fig. 1) are first evacuated and the charcoal H baked for half an hour during evacuation, to drive out all adsorbed gases, especially helium. After the charcoal has cooled down, the stopcocks F and G are closed and bulbs A and C evacuated alone through D and E. When the peroxide solution begins to boil and dissolved air is evolved, the iron bar attached to the platinum black is moved by a magnet to lower the platinum into the solution. A vigorous evolution of oxygen takes place, which flushes out remaining air from the peroxide and also the concentrated sulphuric acid in C. This is to dry the oxygen, and valve B functions as a non-return valve should acid accidentally suck back.

Though one would expect, because of the larger bubbles produced, that continuous evacuation while the oxygen is being evolved would be a more rapid method of ridding the peroxide of dissolved air, it must be remembered that the gas space above the solution will contain some helium, and the total pressure of this gas space is always a few mm. of mercury even during evacuation.

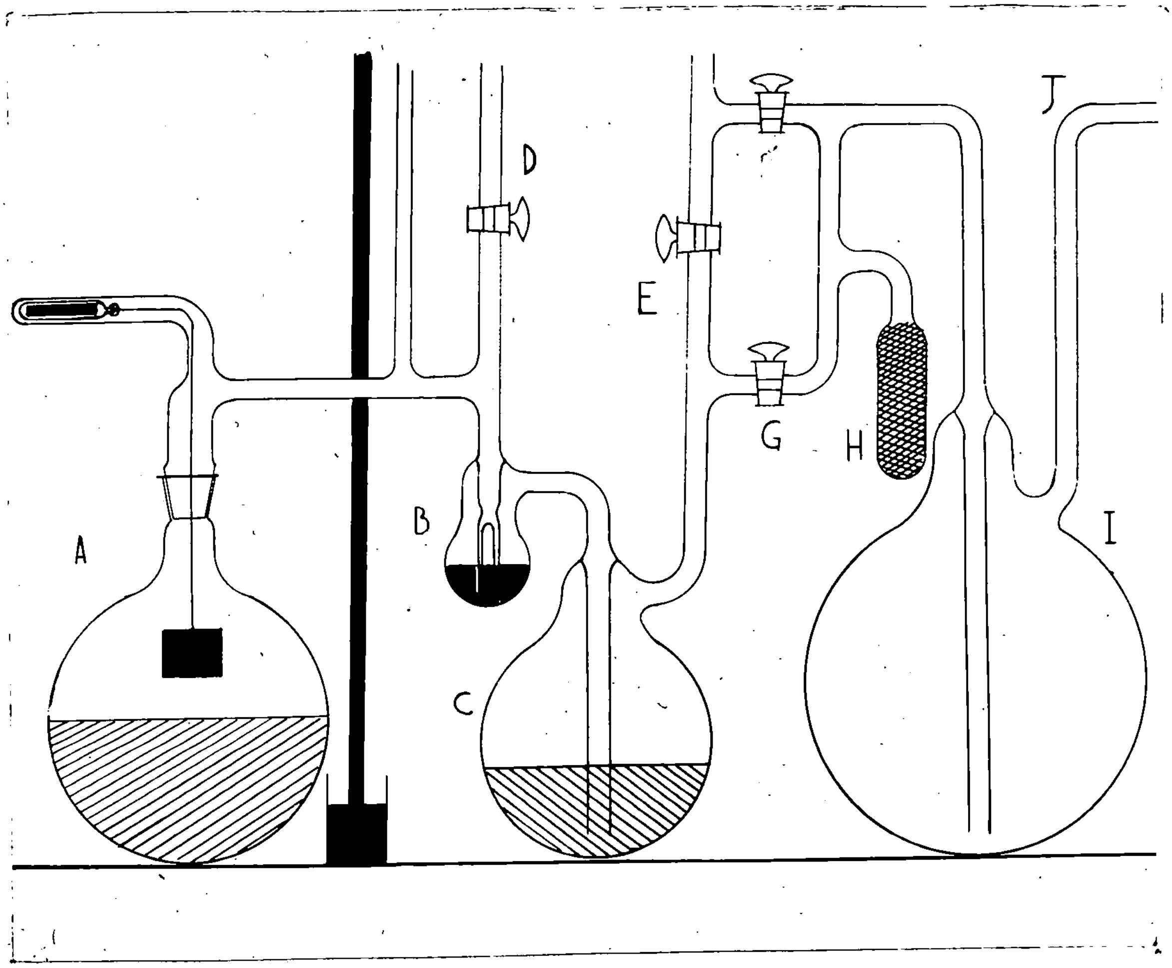


Fig. 1.

The helium in this will maintain a partial pressure which will gradually be reduced on evacuation, as the rate of evacuation is greater than the rapidity with which the helium will redistribute itself throughout the gas space. As long as there is an appreciable pressure of gas in this space, so will there be a partial pressure of helium, and the greater that volume, the longer the evacuation will have to continue to reduce the partial pressure of helium to a negligible quantity. Consequently for a rapid removal of helium, it was found better to continue oxygen evolution until a pressure of about 10 cms. was built up, and then rapidly evacuate this gas, at the same time ceasing oxygen production. Performing this operation half a dozen times is quite sufficient to rid the whole apparatus of helium.

When the flushing is complete, stop-cock G is opened and the oxygen collected in storage bulb I. Thanks to the diffusion of helium through glass and the liberation of dissolved helium from the glass when the pressure inside the glass is much less than atmospheric pressure, it is necessary to repurify the oxygen once a week, by adsorbing it on charcoal cooled with liquid oxygen and evacuating the system for approximately half an hour.

2. LIBERATION AND PURIFICATION OF HELIUM.

A typical experiment involving every part of the Helium Apparatus is the extraction of helium from a meteorite. Original work with meteorites necessitated a few grams of the substance; it is now possible to determine the content in only a fraction of a gram, usually about 0.1 gram. The most suitable solvent for the meteorite is sulphuric acid approximately 5 N and saturated with potassium persulphate. Use of acid of greater concentration and in the absence of persulphate tends to produce passivity in a short space of time, and even warming the solution fails to dissolve the meteorite within

12 hours. The saturated solution must be freshly prepared, otherwise decomposition of the persulphate will have occurred and the iron will become passive.

The meteorite drillings occupy the small closed side tube of the dissolving vessel A while acid in the vessel is being flushed clear of air by electrolysis (Fig. 2). Then by means of a magnet the drillings are transferred to the solvent, when a brisk evolution of hydrogen takes place. Approximately 10 cms. pressure of pure oxygen is introduced at this stage through stopcock B and a current passed through the heating coil until the latter just commences to glow. Hydrogen burns quietly here unless the oxygen pressure approaches about 20 cms. Depending on how fine the drillings are and the presence or absence of grease, it is usually possible to dissolve the whole within half an hour. Initial warming of the solution by hot water around the vessel assists in starting a rapid dissolution.

It is impossible to remove all traces of hydrogen in A and unless it is totally removed (i.e. less than 10^{-9} cc. remain), its presence will effect the measurement of the inert gases. Catalytic burning of hydrogen with oxygen by circulation through a heated palladium furnace proves the simplest and most effective method. Gas from the dissolving vessel is therefore flushed into the circulating part of the apparatus by lowering the mercury in the ventil D until it just lips the bend, cooling charcoal H with liquid nitrogen or oxygen and slowly opening stop-cock C. To ensure complete removal of helium from the vessel, five quantities of oxygen each of about 10 cms. pressure are used and at the same time the sulphuric acid is electrolysed to drive out dissolved helium. The ventil functions as a non-return valve, preventing back diffusion of helium. Once all the helium, oxygen and remaining hydrogen have been flushed into the circulating chamber, ventil D is

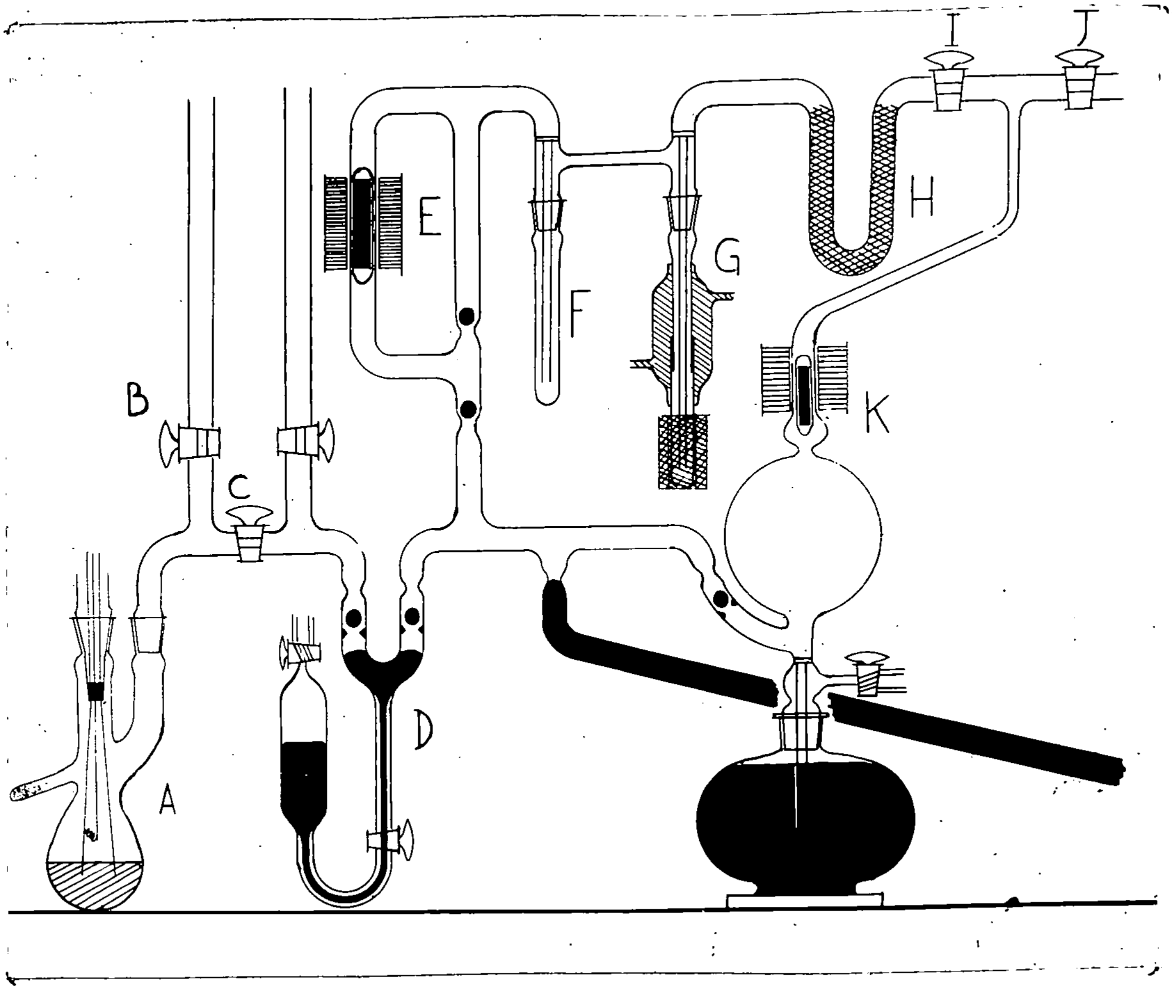


Fig. 2.

closed and the Dewar removed from charcoal H. The palladium furnace G and the circulating pump E, which is a metal bar and sollenoid actuated by a make-and-break motor system, are switched on. Circulation is continued for approximately 20 minutes which is sufficient time to remove all traces of hydrogen from the mixture.

The only gases which now remain are helium and oxygen and if an air leak has occurred at some stage during the experiment, an equivalent amount of neon. The whole is transferred to the fractionating column by first closing stop-cock I and then slowly opening stop-cocks J. The remaining helium in the glass tubing to the left of stopcock I is pumped into the fractionating column by Toeplering about five times, i.e. raising the mercury beyond the sollenoid, dropping the valve K by switching off the sollenoid, and lowering the mercury. Some of the latter is retained by the valve, consequently creating a vacuum in the bulb of the Toepler into which more of the gas from the side-tubes will expand. In order that the gas space before the fractionating column be as small as possible, the mercury is raised practically to stop-cock J.

3. FRACTIONAL ADSORPTION OF HELIUM AND NEON ON CHARCOAL.

A comprehensive survey of the theoretical aspects of fractional adsorption and desorption as well as the practical applications of helium and neon separation has been outlined by Glueckauf (G3), and so nothing more than a brief summary of the theory plus an account of the operation of the fractionating column of the Helium Apparatus is necessary here.

A gas will distribute itself between an adsorbent and a gas space, the quantity adsorbed depending on the quantity of adsorbent, the volume of the gas space, the temperature of the adsorbent and the adsorption coefficient of the gas in question. Using two gases of different adsorption coefficients, an optinum ratio of the quantity of the adsorbent to the volume of the gas space will exist for a maximum separation of the two gases. Such an optinum condition occurs when the ratio of the gas space to the quantity of adsorbent equals the square root of the adsorption coefficients, and when the sum of the distribution factors equals 1

(1) $V/S = \sqrt{\alpha\beta}$

(2) $a + b = 1$ where $a = \dfrac{1}{1 + \alpha\frac{S}{V}}$

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

With this data, it is then possible to calculate the number of adsorption units to give the desired degree of separation, and also the number of fractional operations necessary for separation.

Glueckauf chose a convenient value for S as 2.5 grams, which corresponds to a gas space of approximately 80 ccs. in theory. This gave optinum values for the distribution coefficients of helium a = 0.769 and neon b = 0.231. The correct number of fractionating units is theoretically 12 and the number of fractional operations to separate helium from neon equal to 2 x 12 = 24 operations. The charcoals of the column are grouped together, for convenience of cooling, into three batches, two of five charcoals and one of two. An extra small bulb of charcoal between C and D (not shown in Fig. 3) functions in a similar manner to the charcoal in the Pirani gauges, i.e. to adsorb gases evolved from tap grease or from the walls of the glass.

Though theoretically one should obtain complete separation of the two gases at the 24th operation, in practice it is difficult to obtain such exact conditions. The capacity of each bulb was not exactly 90 cc., and in order

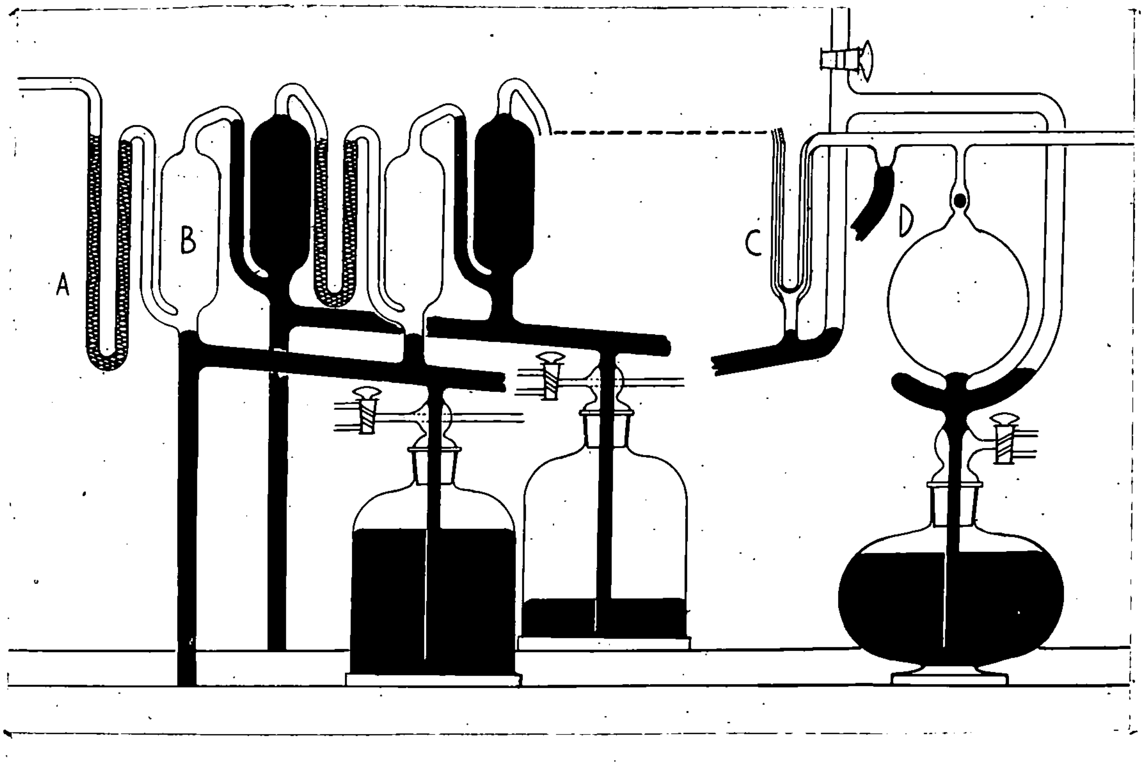


Fig. 3.

to retain oxygen or other carrier gas in the column but allowing neon to pass through after measurement of helium, it was found better to have a longer charcoal U-tube and a correspondingly larger bulb at the beginning of the column. However, a check on the distribution can easily be obtained by fractionating pure helium or pure neon in turn, and calculating the percentage of each coming over outside the limits.

The column is operated in the following way :-
all gases except most of the helium and part of the neon are adsorbed on the first charcoal A (fig. 3). When the mercury is lowered below the side-tube, the rare gases helium and neon will distribute between the charcoal and the gas space, bulb B. Raising the mercury in the front column and lowering that in the rear bulbs transfers the gas to the rear bulbs; then raising the mercury in the rear bulbs and lowering it in the front transfers the gas to the second charcoal - this is one complete operation. The bulbs function as Toepler pumps. At the thirteenth operation the first fraction of helium expands from the capillary tubing C into the large bulb D. The same applies to subsequent operations, then the mercury in the bulb is raised to compress the helium into a standard volume ready for measurement with the Pirani gauges, in the same manner as described in the next section.

So that unnecessary operations are avoided in the fractionation of the neon, the first Dewar is lowered to just cover the bend of the first charcoal after the seventeenth operation, the last batch of helium having passed the fifth charcoal. Then after the twenty-second operation, the second Dewar is removed altogether. After measurement of the helium, the last Dewar is lowered to that the liquid nitrogen just lips the bends of the charcoal-- this will prevent any nitrogen or oxygen entering the Pirani space should the level of liquid nitrogen become too low at some stage in Dewar 1. A further

25 to 30 operations usually suffices for complete removal of neon.

4. PIRANI GAUGES.

The present design of the Pirani gauge used on the Helium Apparatus is indicated in fig. 4. It is the design of Dr. W.J. Arrol once a collaborator of Professor Paneth's. For high sensitivity and stability it is essential to have as small a gas space as possible and at the same time maintain a constant temperature. Hence the shape of the gauge with the essential gas space at the bottom which when in use, is covered to a depth of 15 cms. by liquid oxygen or nitrogen. The compartment above the internal seal through which the leads to the Wheatstone bridge traverse, is evacuated prior to installation, to prevent spurious temperature effects by conduction and convection if air were present. Small pieces of charcoal safeguard the gauge from gases like hydrogen released by glass walls or by stop-cock grease, and gold shavings prevent mercury vapour from attacking the soft soldered leads. A fine nickel wire approximately 30 cms. in length is soft-soldered to tungsten filaments sealed through the internal seal. The wire, in the shape of a W to conserve space, is held taut over a supporting glass rod by means of a tungsten spring. Two identical gauges are employed, one of which A is permanently under vacuum and only present for compensating purposes, and the other B is the working gauge. They form two arms of a Wheatstone Bridge network in conjunction with a resistance box and a sensitive moving-coil galvanometer. A potential of 1 volt is applied to the gauges when in use.

When gas at very low pressures enters the lower evacuated space of the working Pirani, the heat wire will lose part of its energy by impact of "cold" molecules upon its surface. The thermal conductivity of the gas is

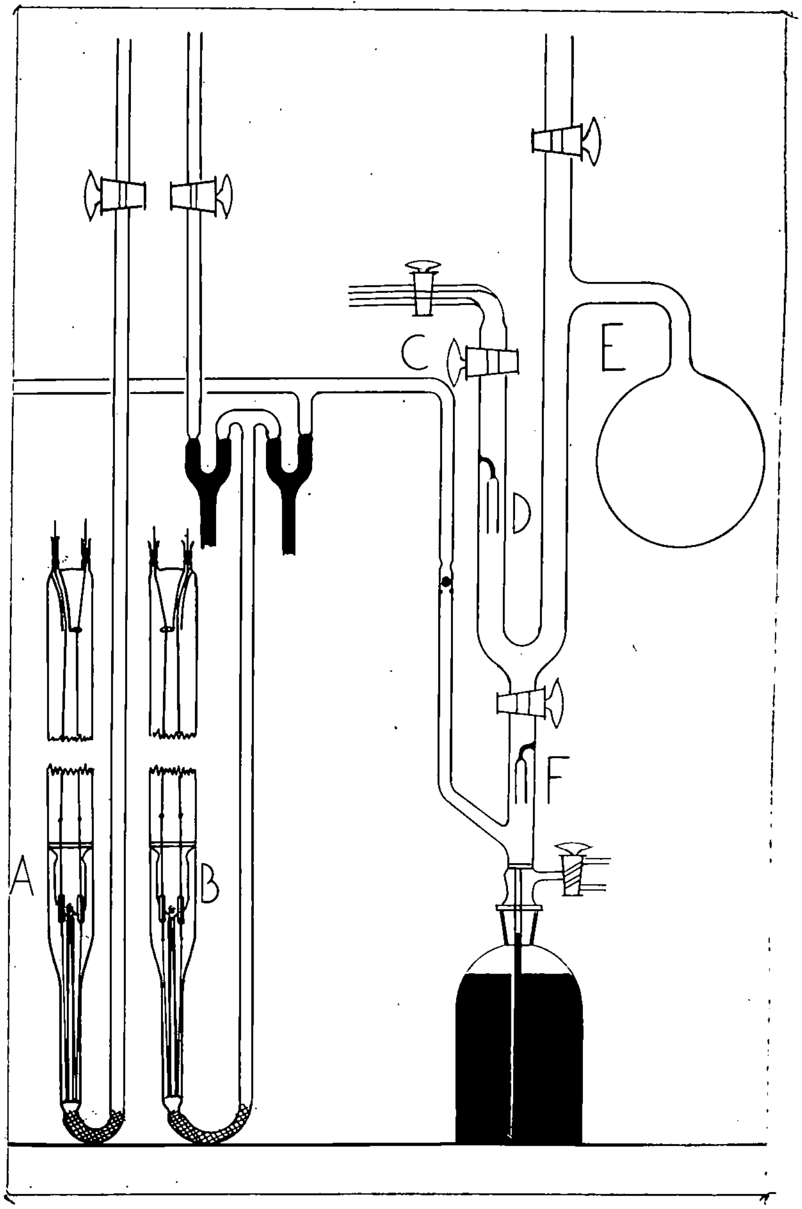


Fig. 4.

proportional to its pressure when the latter is small. Consequently, the resistance of the wire will change and the galvanometer spot be deflected a certain distance. The latter will be a measure of the gas introduced and bears a linear relationship to the pressure. Sensitivity naturally depends on the gas employed. In all our experiments only pure helium or neon entered the gauge and thus calibration was only necessary for these two gases.

To calibrate the Piranis, a known volume of helium or neon is introduced from the calibration apparatus. Here mercury is raised to C and the latter opened to a reservoir of He or of Ne. The mercury is lowered beyond D and raised gently until the meniscus barely touches the lip of the cup. A pressure reading is taken with a cathetometer, the right hand limb of the U-tube being open to the vacuum pumps. This cupful of gas at the pressure just measured is trapped by raising the mercury once again beyond stop-cock C and closing same. Expansion of this cupful of gas into the large volume E and below cup F is accomplished by lowering the mercury again. Cupful F of this gas is then trapped and the gas space above it evacuated, before re-expansion of this gas into the large volume again. Cupfuls of this last expansion are now suitable for calibration.

The exact volume of the gas introduced into the gauge is determined as follows :-

Volume of pipette D = 1.0313 cc.
Volume of pipette F = 1.0141 cc.

The volume of the expansion space had been determined before the apparatus was constructed as shown in the diagram and was found by comparing the pressure of gas in bulb E (volume = 48.082 cc.) with the pressure exerted by this bulbful when expanded into the whole space.

This ratio = 9.385.

Therefore, expansion space $= 9.385 \times 48.082 - 48.082 = 403.15$ cc.

1.0313 cc gas (in D) at pressure p mm, is equivalent to

$P/760 \times 1.0313$ cc. at 760 mm pressure.

When expanded into volume 403.15 cc. and 1.0143 cc. taken, this is equivalent to

$$\frac{P}{760} \times 1.0313 \times \frac{1.0141}{403.15} \text{ cc. at 760 mm. pressure.}$$

This volume is again expanded into 403.15 cc. and 1.0141 cc. taken, equivalent to

$$P/760 \times 1.0313 \times \left(\frac{1.0\overset{141}{313}}{403.15} \right)^2 \text{ cc. at 760 mm. pressure.}$$

The temperature correction is

$$273/T = \frac{273}{293 + (t-20)}$$

$$= \frac{273}{293} \left(1 + 1/293\,(t-20)\right)$$

$$= \frac{273}{293} \left(1 - .0034\,(t-20)\right)$$

Therefore, final volume of rare gas introduced into the Pirani is

$$P/760 \times 1.0313 \times \left[\frac{1.0141}{403.15} \right]^2 \times \frac{273}{293} \left(1 - .0034\,(t-20)\right)$$

or $\quad V \text{ ccs.} = P \times 8.0006 \times 10^{-9} \times \left(1 - .0034\,(t-20)\right)$ cc.

when P is mm Hg and t is °C.

During our experiments on air analysis, we used the gauges over a less sensitive range than hitherto and in order that a reasonable deflection be obtained during calibration we found it necessary to use not only the gas trapped in cup D but also the gas above it to stop-cock C. This volume was determined by taking a pressure reading with mercury touching the lip of the cup, trapping this gas by raising the mercury above the tap and then expanding this cupful into the space above the cup. The ratio of the two pressures gave the ratio of the volume of the cup to the totalvolume above the lip of the cup.

In an attempt to discover why out results on air analysis were so variable individually, we decided to re-check every part of the apparatus including the calibration of the galvanometer scale. This was done by using a standard 5 ohm resistance in parallel with one of the one ohm reistances of the bridge circuit. Switching in this resistance produced the same effect as letting in helium into the gauge. Deflections were taken over all ranges of the scale, and it was discovered that using a deflection of about 10 cms. on a 50 cm. scale, readings at each end were about 6 per cent greater than in the centre of the scale ! So unless calibrations were performed over the same distance of the scale as used when measuring the helium and neon, results could not in general be concordant.

A graph was therefore drawn of deflection against range, a parabolic curve fitted by a least squares method, and a correction table calculated which gave the correction to be applied to any reading between given limits.

We could thus reduce any reading to what would have been read on a perfectly "linear" scale.

--- CHAPTER 3. ---

CHAPTER 3.

REDETERMINATION OF THE DISINTEGRATION CONSTANT OF URANIUM I.

1. INTRODUCTION.

All calculations of geological age by the radioactive method necessarily involve the disintegration constant, or the half-life value, of the disintegrating element. In connection with our work on the ages of rocks and meteorites, using the classical helium method, we have attempted to obtain a reliable figure for the disintegration constant of uranium by measuring the helium generated as α-particles in a known time by a known amount of uranium. This method has previously been used by Günther (G5) who stored solutions of uranium nitrate, originally free from helium, for periods up to three years and then measured the helium produced. Since these experiments were carried out, significant improvements in technique have been achieved, and in the present experiments uranium solutions were kept for only two or three weeks. This greatly reduces the chances of accidential leakage and eliminates the risk of helium diffusing through the walls of the glass vessel containing the solutions.

During the later stages of our research on this subject, we were fortunate in receiving from I.C.I. Widnes, extremely pure uranium metal, whose date of purification was known. The metal could of course, be left in the open air for any length of time without any leakage of helium from it or diffusion of air into it; this eliminated the rather troublesome difficulty of storage of solutions in perfectly air tight apparatus.

Gunther's value of the disintegration constant is approximately ten per cent higher than that reported by Kovarik and Adams (K1), who quote

λ UI $= 1.520 \times 10^{-10}$ years^{-1} (corrected by Nier see later).

This figure has been confirmed by Yagoda and Kaplin (Y1).

λ UI $= 1.52 \times 10^{-10}$ years^{-1} (also corrected by Nier).

Kovarik and Adams used a counting method with a thin film of uranium oxide, U_3O_8, on an aluminium plate as the source of α-particles, in an ionisation chamber. In order that the observed count could be corrected to the theoretical one hundred per cent geometry, they used a grid plate of brass drilled with identical channels according to a set pattern over the source. Counts were taken with the grid in various positions.

Yagoda and Kaplin detected and counted the α-particles from a thin film of U_3O_8 using a fine grain photographic emulsion.

Both these methods are in a sense modern versions of Rutherford's original work in which the rate of α-particle emission from a known quantity of U_3O_8 was measured by observing the scintillations produced on a zinc sulphide screen. (G1.) In view of the known technical difficulty of this method, this value

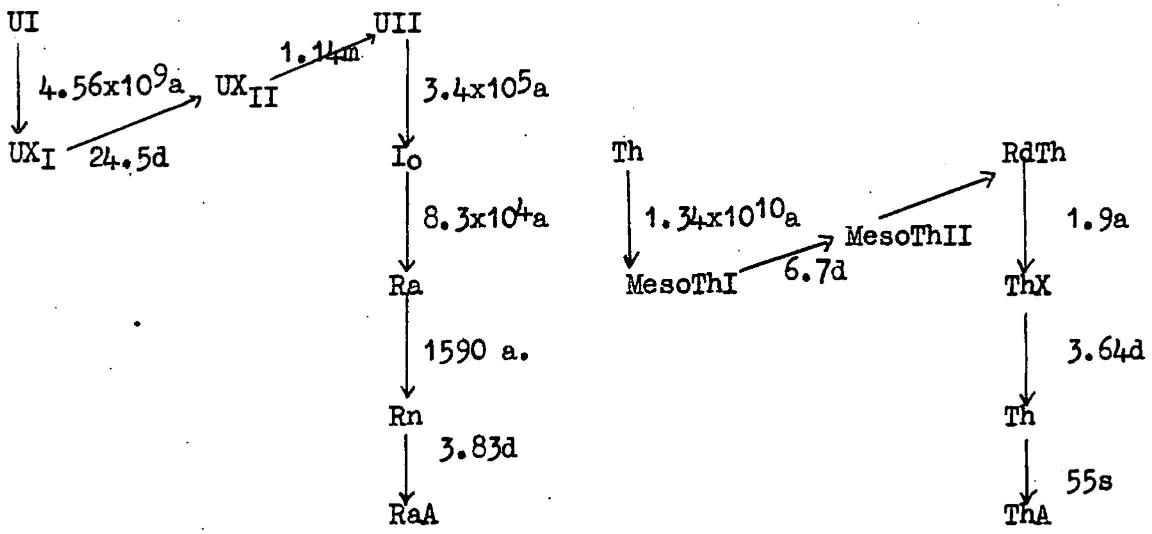
λ UI $= 1.48 \times 10^{-10}$ years^{-1}

is sufficiently close to the value given above.

These are to be compared with Günther's value of

λ UI $= 1.74 \times 10^{-10}$ years^{-1} (corrected in the same way as Kovarik and Adams).

Günther himself suggested that the discrepancy might be due to his failure to purify the uranium from thorium, and more particularly its disintegration products. Most uranium minerals contain thorium, but when purifying the uranium it is not sufficient merely to purify from thorium, but also to extract the meso-thorium I (radium isotope). Meso-thorium I, while not an α-emitter itself gives rise to meso-thorium II, which in turn gives radiothorium, both by β-particle emission. The latter element, a thorium isotope, emits α-particles. Since the half-life of meso-thorium I is 6.7 years and meso-thorium II is 6 hours, while the experiment itself lasts 3 years, it is obvious that too much helium will be found unless meso-thorium I is rigorously excluded.



Günther did carry out a barium precipitation which would remove meso-thorium I, but he failed to purify from thorium, hence both the latter and radio-thorium might have been present, and if so would have accounted for the excess helium he discovered. In our experiment we have adopted the method of extraction with ether, in which uranyl nitrate is fairly soluble. Uranium X and other isotopes of thorium are not soluble and are removed in the aqueous layer.

The percentage of actino-uranium, U^{235} in uranium salts was not known when Rutherford, Kovarik and Adams, and Gunther made their determinations of the disintegration constant. They therefore assumed that all the α-particles counted derived from Uranium I and Uranium II. Actually this is not so; hence the correction applied by Nier which was mentioned above. Neir determined the ratio of AcU to UI plus UII to be 1 : 139 by mass spectrographic means (N1). He estimated that the ratio of activity of the actinum series to that of the uranium series to be about 4.6 per cent. This means that

$$\frac{4.6}{204.6} \times 100 = 2.3 \text{ per cent.}$$

of the observed α-particles come from AcU and 97.3 per cent from UI and UII. On the other hahd, the weight of UI and UII is (I - I/139) 100 = 99.3 per cent of the total; therefore the actual rate of helium production by the UI and UII alone is $\frac{97.3}{99.3} \times 100 = 98.0$ per cent of the apparent rate. In addition the value by Kovarik and Adams has to be corrected for the change in the accepted atomic weight of uranium from 238.12 to 238.045 and in the electronic charge from 4.77×10^{-10} e.s.u. to 4.80 e.s.u.

Attempts have been made by Kovarik and Adams (K3) to obtain the relative activity of the actino-uranium by the "step-method" employed in their determination of the disintegration constant of thorium (K2+). The method utilises the fact that the ranges and energies of the α-particles emitted by some elements differ so much from each other, that it is possible to absorb them selectively by varying thicknesses of aluminium plates. It would therefore be possible to stop the α-particles from Uranium I and Uranium II by aluminium foils leaving those from actino-uranium to be counted alone. Though the method was applied in this case, the apparatus was unfortunately affected by changes in atmospheric pressure, so the results were not very accurate. They did show, however, the ratio of activity of the actino-uranium to the uranium to be of the order of 5 per cent.

2. METHOD.

(a) Employing Uranium Nitrate Solutions.

The specific property of uranium nitrate being fairly soluble in ether was first recorded by Crooks (C6).

Gratias and Collie utilised this method when they determined the half life of Uranium II (G4,G5). When the crystals of uranium nitrate $UO2\ (NO_3)_2\ 6H_2O$, are shaken up with ether in a separating funnel, the water of crystallisation forms an adequate amount of aqueous layer in which all impurities, especially meso-thorium I and thorium will dissolve. This layer can be discarded once all the crystals have gone into solution and the whole thoroughly shaken up. It is not necessary to add a further quantity of water to ensure thorough purity when "Analar" crystals are employed.

The uranium nitrate is then extracted with pure water, and the ether boiled off before the solution is suitable for the experiment. Well over one hundred years will elapse before the quantity of Ionium, also an α-emitting element produced by the dinsintegration of Uranium II will make a possible error or more than 0.1% of the total α-particles emitted. Consequently, repurification during the course of the experiment was unnecessary.

With the uranium nitrate solution in the main flask of the uranium apparatus, all dissolved air and helium is removed by flushing through with electrolytic gas and the apparatus left under vacuum for two or three weeks. The helium produced as α-particles by disintegration of the uranium is then flushed out with electrolytic gas again, and collected in a small receiving vessel, where the hydrogen/oxygen mixture is burned at an electrically heated platinum coil. Purification and measurement of the helium is then accomplished by the Helium Apparatus.

It is essential that all experiments with helium be performed in apparatus made of soda glass, because of the ability of the gas to diffuse relatively rapidly through hard glasses like pyrex. A certain amount of helium will diffuse through soda glass when under vacuum. The most appreciable source of excess helium, however, is the adsorbed helium released into a vacuum from glass. Gunther, in his experiments, used flasks of similar capacity to ours, and found that 3×10^{-7} cc. helium diffused into his blank apparatus in 1142 days e.g. approximately 3×10^{-10} cc./per day. In three weeks, that would mean about 6×10^{-10} cc. helium, or within one per cent of the amount of helium produced by disintegration. Release of helium from minerals and glass is also greatly accelerated by the presence of hydrogen, and therefore the initial flushing of the solution with electrolytic gas will replace most of this dissolved helium. (C4.)

Experiments on the actual rate of diffusion of helium through glass and minerals have been performed by Paneth and Rayleigh. Paneth quoted 10^{-16} cc./cm2/hour as the amount of helium which diffused through soda glass (P10,R3).

(b) EMPLOYING URANIUM METAL.

Because the date of purification of the uranium metal was known, the volume of helium present within a known weight of the sample will give the disintegration constant of the metal. As a recheck on the date of purification, however, the sample could be left for a further two months or so and the volume of helium once more measured. From the difference in the helium contents, and knowing the time and weight of the sample dissolved, the disintegration constant could be calculated. With this method, it is not necessary to maintain a perfect vacuum for more than the time required to dissolve the sample.

A very convenient solvent for this experiment is a saturated solution of potassium cupric chloride ($2KCl,CuCl_2.2H_2O$). Such a solution is capable of dissolving a 20 gram sample of uranium metal within half an hour. Hydrogen is evolved during the process and can be used to displace the helium into the burning chamber attached to the Helium Apparatus, where the hydrogen is burned with pure oxygen, and the helium measured in the normal way.

Dissolution of the uranium is rapidly increased when the solution is warmed to about 60°C. The uranium first displaces copper from the cupric chloride; and the presence of the potassium chloride aids the solution of the copper, probably on account of the formation of a double salt.

$$U + 2CuCl_2 = UCl_4 + 2Cu$$

$$Cu + CuCl_2 = Cu_2Cl_2$$

Treadwell (T1) recommends using a small percentage of concentrated HCl with the double salt when dissolving metals like iron. We found the reaction just as rapid without the acid.

3. EXPERIMENTAL.

(a) PREPARATION OF SOLUTIONS.

Approximately 500 grams of "Analar" uranium nitrate ($UO_2(NO_3)_2.6H_2O$) were shaken up with ether, and when all crystals had dissolved the aqueous layer was separated. The pure uranyl nitrate etherial solution was then extracted with distilled water to transfer most of the nitrate to the aqueous layer. The latter was then boiled and stirred vigorously to evaporate the dissolved ether. After making up the solution to 1000 ml., gravimetric analysis was carried out on 1 ml. portions of the solution. They were slowly evaporated to dryness, strongly ignited with a Mecker burner and heated to constant weight. The nitrate in this way was completely converted to uranium oxide U_3O_8.

Solution. 1.

Wt. of crucible I (const. weight) = 11.9530 gms.

" " " I + U_3O_8 = 12.1510 gms.

Wt. of U_3O_8 = 0.198 gm.

Wt. of crucible II = 10.8790 gm.

" " " II + U_3O_8 = 11.0790 gms.

Wt. of U_3O_8 = 0.200 gm.

1 ml. uranyl nitrate solution = 0.199 gm. U_3O_8

(M.W. of U_3O_8 = 842.2, M.W. of $UO_2(NO_3)_2.6H_2O$ = 502.1)

Now 842.2 gm. U_3O_8 are equivalent to 3 x 502.1 gm. uranyl nitrate

0.199 " " " " " 0.356 " " "

∴ 1000 ml. uranyl nitrate solution contains 356 gm. $UO_2(NO_3)_2 6H_2O$

(5 ml. were removed for the gravimetric analysis i.e.

5 x 0.356 = 1.780 gm.)

Amount remaining in solution = 354 gms. uranyl nitrate crystals.

Solution II.

Calculated as above, this solution contained 278 gm. uranyl nitrate.

Two solutions were originally prepared, and later when the apparatus was modified, a further quantity was made up and divided between the above two solutions.

Solution III, contained 428 gm. uranyl nitrate.

Thus the two solutions contained the following amounts of uranium nitrate

Solution I ≡ 568 gm. uranyl nitrate ≡ 270 gm. uranium.

Solution II ≡ 492 " " " ≡ 233 " "

(b) INITIAL EXPERIMENTS WITH NO. 1. APPARATUS.

(i) DESCRIPTION AND USE OF APPARATUS.

Fig. 5. outlines the first apparatus designed for the production and collection of helium from uranium nitrate solutions. It was kept entirely separate from the Helium Apparatus in case of accidental radioactive contamination of the latter. Like the Helium Apparatus it was constructed entirely in soda glass.

A is the electrolyser containing a solution of 5 N sulphuric acid and platinum foil electrodes. B is the main flask half filled with the uranium

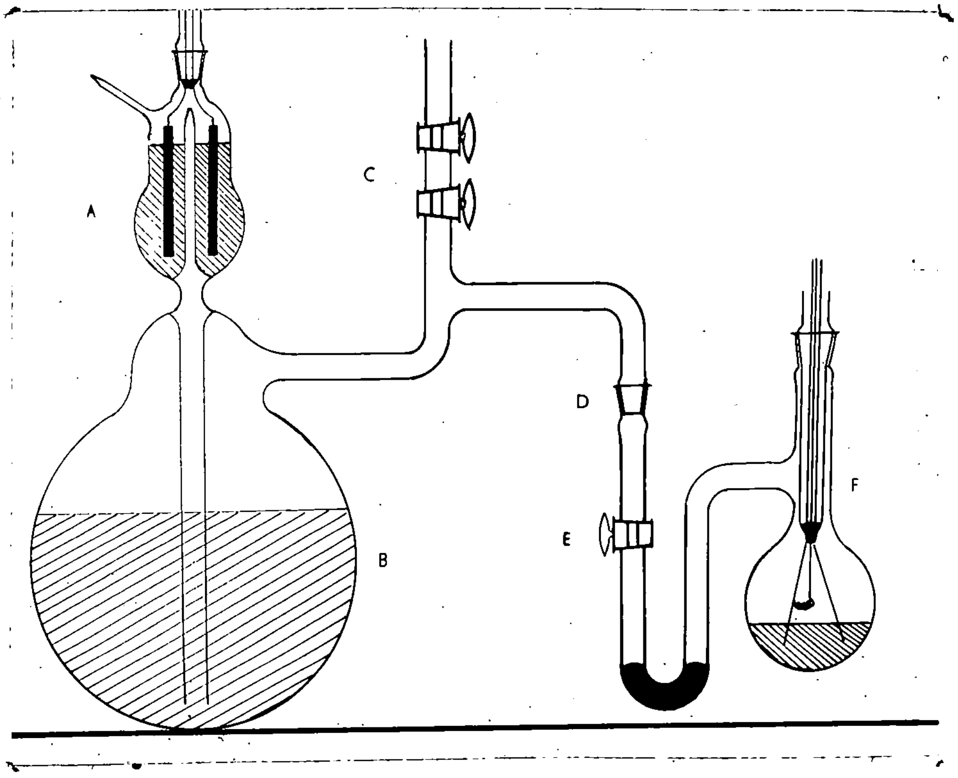


Fig 5.

nitrate solution (approximately 1000 ml.) F is the receiving vessel where the electrolytic gas is burned and the helium collected. It is detachable at cone D for re-attachment to the Helium Apparatus.

The apparatus was evacuated by opening stop cocks C slowly to the rotary pump. Electrolysis was begun in both A and F to flush out dissolved air from the sulphuric acid and nitrate solution. Because of the small volume of F (20 cc.), only 10 minutes of electrolysis was sufficient to displace all helium from this vessel and the sulphuric acid, but electrolysis of A and flushing of B was continued for a further two hours. Helium very easily diffuses backwards, but if electrolysis is carried out in batches, i.e. electrolysing until a pressure of say 10 cms. mercury has built up, and then rapidly evacuating and repeating the process about ten times, complete removal is ensured.

After 24 hours, a blank was carried out to test the apparatus for leaks. The apparatus, itself, in the absence of the solutions had been tested beforehand by leaving under vacuum for 48 hours - a Tesla coil discharge indicated the absence of any noticeable leak. Helium from the uranyl nitrate solution was displaced by electrolytic gas from A. With stop-cock E open, and a small current passed through the platinum coil until it just glowed, the electrolytic gas bubbled past the mercury shown in the diagram. This functioned as a non-return valve, and the reduced pressure in F was maintained by the burning of hydrogen and oxygen. Two hours of electrolysis produced a volume of electrolytic gas more than ten times the volume of the solution, a sufficient quantity to thoroughly remove all traces of helium from the nitrate. E was then closed, and to avoid uranyl nitrate being forced into A when the collecting vessel was removed, air was introduced first by snipping the small capillary protruding from A.

On attaching the collecting vessel to the Helium Apparatus and once more passing a current though the heating coil to burn any residual hydrogen, it was noticed that, on opening E to the vacuum, an excessive volume of gas bubbled past the mercury, and indicated a pressure in F higher than that of water vapour alone. This would be satisfactorily explained on the basis that oxygen would dissolve preferentially to hydrogen in B, leaving an excess of hydrogen to be swept into F.

Two stop-cocks C were employed to decrease the possibility of air leaking into the apparatus via the pump.

(ii) OBSERVATIONS AND MODIFICATIONS.

If the first four complete experiments, the amount of helium obtained was much smaller than would be expected from the accepted value of the uranium half-life. This was partly explained by the increasing pressure in F, to which reference has already been made, which made it impossible to flush out the solution thoroughly towards the end of the experiment without using dangerously high pressures. This effect was overcome somewhat by burning the electrolytic gas continuously instead of in batches as was first planned. This method ensured better stirring of the solution because of the larger size of bubbles at the reduced pressure. It had the disadvantage, however, in not removing the helium from the gas space so efficiently as in the batch method.

At one stage in the experiments, it was thought that a smaller gas space above the solution would assist in giving a more rapid and complete removal of helium from the uranium. But the increase in volume necessitated a more rigorous original evacuation, and after many accidents had occurred at the intial stages of evacuation and electrolysis, we returned to the idea of having a gas volume approximately half the volume of the solution.

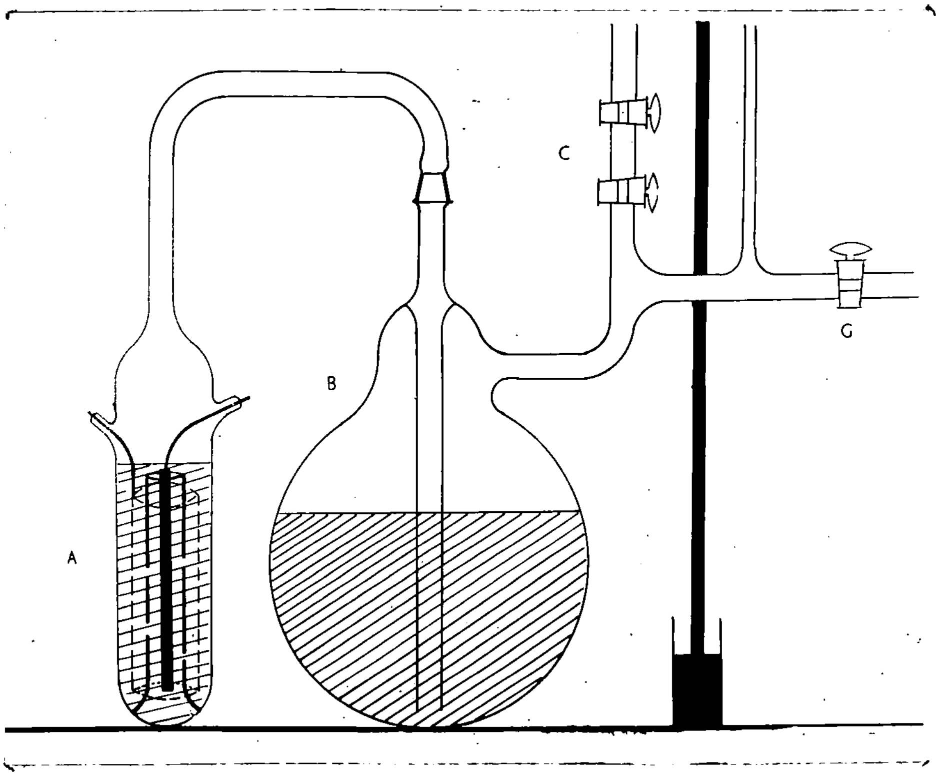


Fig. 6.

Another great improvement was the replacement of the collecting vessel by one of much larger capacity. Whereas with the small flask of 20 cc. volume a pressure of 10 cms. hydrogen in excess of oxygen was built up within three quarters of an hour of electrolysis, because of the differences in solubilities, with the larger flask of 50 cc. capacity, the pressure even after two hours electrolysis was sufficiently small so as not to decrease the rigorous stirring effect. Consequently flushing out of the solutions became more thorough and carried out in a shorter time.

The experimental results were, however, invalidated by the fact that large amounts of neon were found with the helium, indicating incomplete removal of air initially, or, alternatively a leak at some stage of the experiment. It is, however, possible that some of the gas measured as neon may have been hydrogen, if the combustion had not been carried to completion in the Helium Apparatus. In later experiments particular care was taken to avoid this possibility.

Three more experiments carried out with the first apparatus produced reasonably reliable results. In each case, however, there had been a slight air leak; but knowing the exact amount of neon present, and the normal ratio of neon to helium in the atmosphere, the corresponding amounts of helium actually due to disintegration was calculated.

(c) EXPERIMENTS WITH NO. 2 AND NO. 3 APPARATUS.

The second uranium Apparatus (Fig. 6) was slightly modified by incorporating a manometer to indicate how quickly the electrolytic gas was being burned, and an additional stop-cock G so that the helium vessel could be removed without introducing air into the main part of the apparatus. This stop-cock was purposely left out of the first apparatus, because of the additional possible source of leakage. The electrolyser was somewhat larger

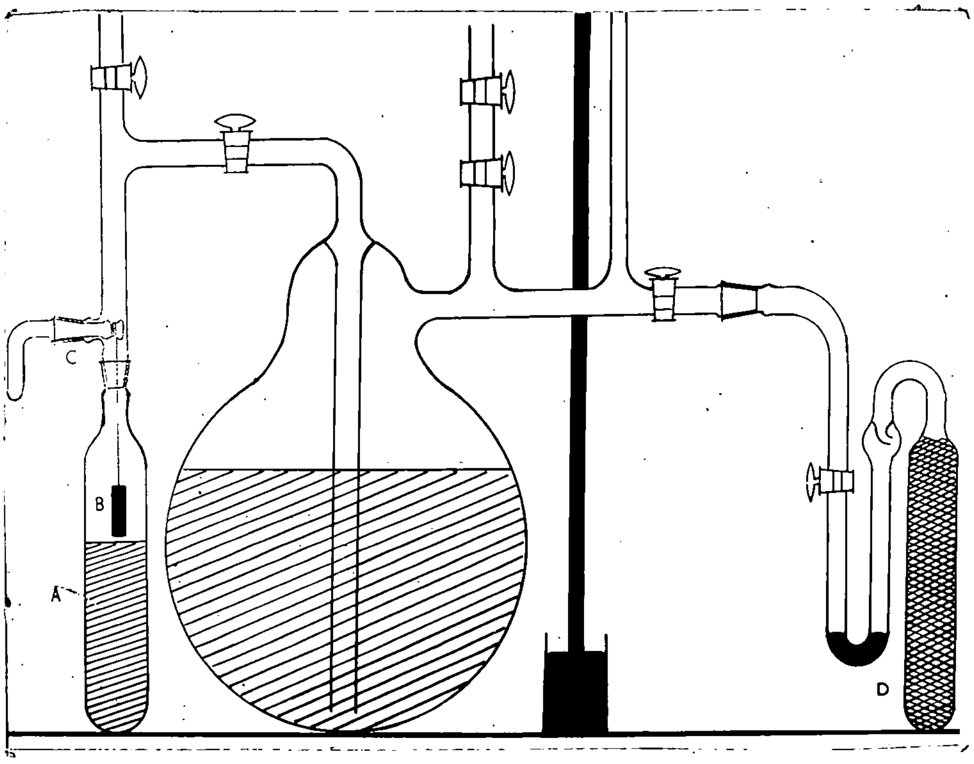


Fig. 7.

and employed nickel electrodes of a more substantial nature than those of Platinum foil, which jerked about during electrolysis, with a danger of shorting. The larger electrolyser also provided a more rapid stream of bubbles through B. With nickel electrodes, a caustic soda electrolyte became necessary.

All experiments with this apparatus gave an excessive helium deflection, and attempts failed to discover the source of the leak. It was abandoned for No.3 apparatus.

The flushing agent was hydrogen, produced by lowering the zinc rod B by means of spindle C into dilute sulphuric acid (fig. 7). Liquid-oxygen-cooled charcoal was used to adsorb the hydrogen and maintain the continuous stream of bubbles through the uranium nitrate solution. D could be detached, fixed to the Helium Apparatus and the hydrogen burned with an external source of pure oxygen leaving the helium to be measured in the normal way. Flushing of the solution, unfortunately, could not be maintained for very long, being limited by the amount of charcoal available in D. In one hour the latter became saturated and during the last quarter of hour, the stream of bubbles being so slow, were far from effective. This apparatus, too, was abandoned for No. 4 which employed electrolytic gas again.

(d) FINAL EXPERIMENTS WITH NO.4 APPARATUS.

With No.4 apparatus depicted in fig. 8, the only part which must remain perfectly air tight during the three week period, is the uranium solution flask and the glass tubing connecting it to the ventils. The remainder of the apparatus could be re-evacuated just prior to the removal of the helium for determination. Two electrolytic flasks were used in series so that a rapid evolution of electrolytic gas could be produced with consequent rigorous stirring of the solutions. The electrolytic gas, carrying the

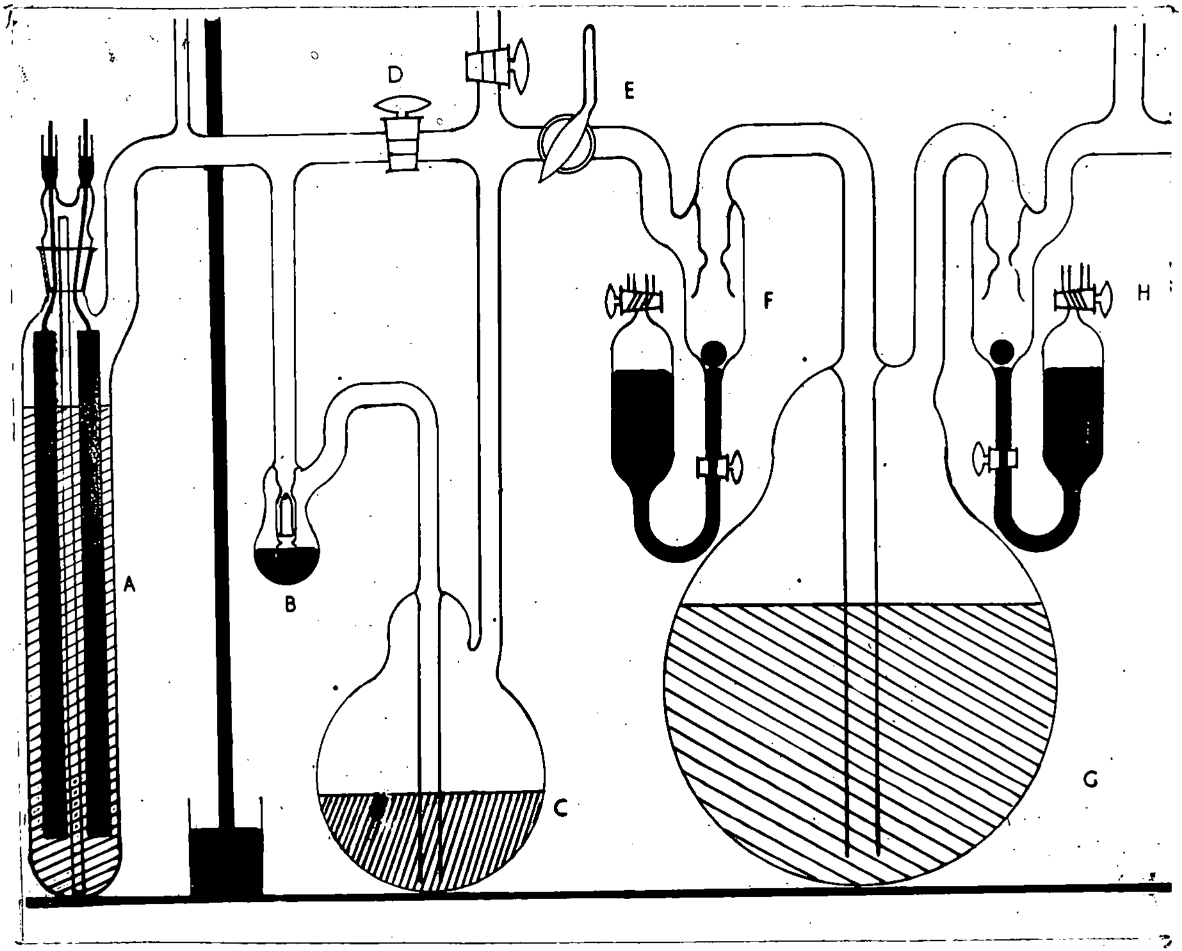


Fig. 8.

helium with it, was burnt in a special combustion vessel which communicated directly with the Helium Apparatus. In order that the gas could be burned quietly at the platinum spiral without risk of sudden explosions, a valve was incorporated which maintained a maximum pressure of 5 cms. of mercury at the burning side of the apparatus. With this low pressure, the rigorous stirring effect could also be maintained. Electrolysis was continued for about two hours before transferring the helium to the circulating part of the Helium Apparatus and measuring the helium in the normal way.

In fig. ~~7~~ 8 only one electrolyser is indicated A. B is a mercury valve to avoid sucking back of the concentrated sulphuric acid from C to A. Water vapour and caustic soda caused stop-cock E to become very streaky and apt to leak hence the flask C with concentrated H_2SO_4 to absorb the water vapour. Ventils F and H of this design allowed an excess pressure against the ball bearing, so that, even though stop-cock E may leak slightly, air would not reach flask B. Also, complete evacuation at both sides of stop-cocks E and similarly to the right of H could be accomplished without evacuating part of the water exerting a small pressure in G.

Several tests were carried out after leaving the solution over-night, but in each case a large amount of helium was measured, which indicated in actual fact a leakage of the order of 10 cu. mm. air per day. In an endeavour to eliminate this, no detectable leak having been discovered in the apparatus, the glass-tubing connecting the uranium flasks to the ventils was coated with wax.

By this time, we had been fortunate in obtaining samples of pure uranium metal, and so experiments were immediately begun with these.

(e) EXPERIMENTS WITH URANIUM METAL.

The apparatus designed for this experiment is shown in Fig. 9.

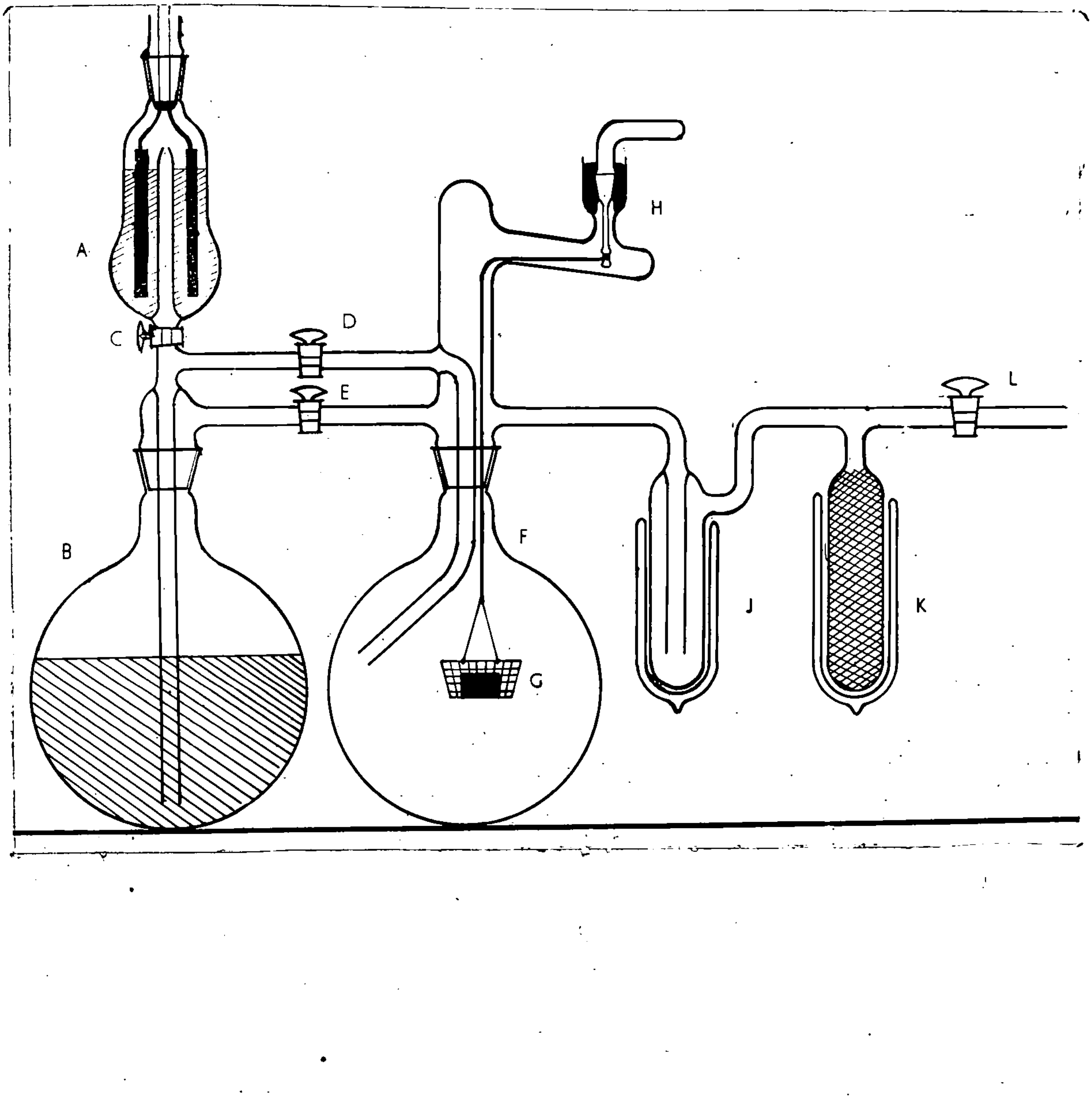


Fig. 9.

Electrolytic gas produced again from sodium hydroxide solution with nickel electrodes was to flush out all air from the potassium cupric chloride solution in flask B. Stop-cocks D and E were then closed and the remainder of the apparatus thoroughly evacuated with the charcoal in K baked at the same time. It was necessary to have the solvent in a separate flask from the uranium to avoid partial dissolution of the latter during the initial flushing of the solvent. Once evacuation was complete, electrolysis was commenced again, and a pressure built up in flask B. With stop-cock C then closed and stop-cock D opened, the pressure of electrolytic gas in B caused the liquid to be siphoned into F. Stop-cock D was then closed again, the water trap J cooled with liquid oxygen to avoid saturation of the charcoal with water vapour and the charcoal tube itself then cooled. The spindle H was turned to lower the uranium suspended in the platinum basket G into the solution. The cone and socket of the spindle were immersed in mercury to avoid any leakage of air past it.

Hydrogen evolved during the rigorous dissolution of the uranium was adsorbed on the charcoal, and later allowed to leak slowly into the burning chamber to be burned with oxygen. When all the uranium had dissolved and most of the helium concentrated in the burning vessel, electrolysis was once more commenced to drive out the helium remaining in the normal way.

Two experiments were carried out using approximately 20 gms. of uranium metal, but in each case a large amount of neon was also present indicating a leak during the dissolution. This may have been due to the cone and socket of the uranium flask warming up so much during dissolution, that air slowly leaked in.

4. RESULTS.

(a) SPECIMEN CALCULATION.

During the course of our experiments we had assumed that a complete separation of helium and neon had occurred at the 25th operation of the fractionating column of the Helium Apparatus. When we carried out the experiments on stratosphere air analysis, we re-checked the helium/neon distribution and discovered that 6 per cent of the neon came over with the helium fraction, and that a further 3.4 per cent came over after the 39th operation, at which operation Glueckauf in his experiments had fractionated all his neon. Our results were accordingly re-calculated.

The results of experiment No. 5 suffice as a specimen calculation.

He deflection (13th to 25th operational incl.) = $\underline{13.60}$ cms.

Ne deflection (26th to 39th " " = $\underline{2.11}$ cms.

The above neon deflection is actually 90.6 per cent of total

$$\text{Total Neon} = \frac{2.11}{90.6} \times 100 = 2.33 \text{ cms.}$$

$$\text{Net\cancel{t} He deflection} = 13.60 - (6\%\ 2.33\ ) = 13.60 - 0.14$$

$$= \underline{13.46} \text{ cms.}$$

The Pirani gauge was known to be 0.636 times as sensitive for neon as for helium, so that assuming the neon to be due to a leak in of air and using the known helium and neon contents of air (5.24 and 18.2 p.p.m. respectively) the deflection of 2.33 for neon would be equivalent to

$$2.33 \times \frac{5.24}{0.636 \times 18.2} = 2.33 \times 0.454 = 1.06 \text{ cms. helium.}$$

$$\text{He from uranium alone} = 13.46 - 1.06 \text{ cms.}$$

$$= \underline{12.40} \text{ cms.}$$

A calibration with a known quantity of helium gave 1 cm. deflection correspond~~s~~ing to 3.38×10^{-8} cc. NT.P.

$$\text{He from uranium} = 12.40 \times 3.38 \times 10^{-8} \text{ cc.}$$

Helium produced by UI and UII alone in 19.0 days (correcting for the AcU as explained previously)

$$= \frac{98}{100} \times 12.40 \times 3.38 \times 10^{-8} \text{ cc. NTP.}$$

$$= \underline{4.10 \times 10^{-7} \text{ cc.}}$$

Now the helium production of 1 gm. uranium in 1 year will be :-

$$2 \times \frac{1}{238} \times \lambda \times 22.4 \times 10^{-3} \text{ cc. NTP}$$ (twice because UII is in equilibrium with UI)

So that 4.10×10^{-7} cc. $= \frac{19.0}{365} \times \frac{2}{238} \times \lambda \times 22.4 \times 10^{-3} \times 270$ cc.

He in 19.0 days from 270 gm. uranium which gives

$$\lambda = \frac{410 \times 10^{-7} \times 365 \times 238}{2 \times 19.0 \times 22.4 \times 103 \times 270} \text{ years}^{-1}$$

$$\lambda = \frac{4.10 \times 10^{-7}}{19.0} \times 0.0718 = \underline{1.55 \times 10^{-10} \text{ years}^{-1}}.$$

$$t_{\frac{1}{2}} = \frac{0.693}{1.55 \times 10^{-10}} = \underline{4.48 \times 10^{9} \text{ years.}}$$

(b) TABLE OF RESULTS.

Experiments.	He Deflection (op.13-25)	Ne Deflection (op.26-39)	Duration of Experiment.	Pirani Sensitivity.	λ UI.	$T_{\frac{1}{2}}$UI.
5.	13.60 cms.	2.11 cms.	19.0 days.	3.38×10^{-8} cc/cm.	$1.55.10^{-10}y^{-1}$.	$4.48.10^{9}$y.
6.	15.62 "	1.80 "	21.0 "	3.38	$1.66.10^{-10}y^{-1}$.	$4.19.10^{9}$y.
7.	11.41 "	6.00 "	12.0 "	3.22	$1.51.10^{-10}y^{-1}$.	$4.58.10^{9}$y.

$$\text{Mean} = \underline{\lambda\,\text{UI} = 1.57 \pm 0.03 \overset{?}{\times} 10^{-10}\ y^{-1}}$$

$$\underline{T_{\frac{1}{2}}\text{UI} = 4.42 \pm 0.08 \times 10^{9}y}$$

(c) DISCUSSION AND COMPARISON WITH LITERATURE.

From the results so far obtained it can be seen that the amount of neon measured is not proportional to the time the apparatus has spent under vacuum and therefore one can assume that the apparatus is not appreciably porous to neon or that a slow leak existed through the glass itself.

Some of the soft glass tubing used in the construction of the apparatus, was very streaky, one or two streaks passing right through the wall of the glass in such a longitudinal fashion that detection with a Tesla coil was impossible. Such capillaries can be closed naturally by heating the tubing before employing it. As a further precaution, the glass can be covered with wax.

However, in later experiments, if the leak had been due to streaky glass, the amount of neon detected would have been proportional to the time the apparatus had spent under vacuum.

Initial flushing of the solutions during the later experiments was quite adequate. There was no necessity to allow air into the apparatus before commencing the next experiment, and to ensure thorough removal of helium, the solution was flushed again before commencing a run. The only conclusion we can arrive at to explain this presence of neon is leakage of air past the stop-cocks during the three weeks or so. It is difficult to believed that a leakage could have occurred when new stop-cocks were employed, especially stop-cocks which were ground before use, one would expect two stop-cocks in series to maintain a good enough vacuum on one side when the space between them was evacuated also.

Though the last apparatus incorporating mercury ventils as a protection against leaks should give the answer to the problem outlined above, absolutely pure uranium metal which can be stored for many months unprotected in any way, is a far more suitable material with which to tackle this problem. The amount of helium which escapes from the surface layer of the metal is negligible compared with the bulk of the sample itself.

It is unfortunate that other more urgent problems have had to be tackled leaving no time for detection of the existing leak in the Uranium Metal Apparatus.

Comparing the mean of our results with that of Kovarik and Adams, we see that it is within 3% of their value, in better agreement than the result of Gunther, whose purification was suspected.

Rutherford and Geiger	1.48×10^{-10}	years^{-1}
Kovarik and Adams	1.520×10^{-10}	"
Yagoda and Kaplin.	1.52×10^{-10}	"
Gunther	1.74×10^{-10}	"
Ours	1.57×10^{-10}	"

CONCLUSION.

Uranyl nitrate solution purified thoroughly from all daughter products of uranium and also of thorium and its daughter products, is a suitable material for determining the half-life value of Uranium I, provided the flask containing the solution is not in contact with any stop-cock or other similar source of leakage. It is necessary to maintain a rapid stream of electrolytic gas bubbles through the solution at a reduced pressure of 5 cms. mercury for two hours or so in the initial evacuation of the vessel and also in the actual displacement of the Helium into the apparatus for measurement.

A far more convenient method for the determination is the utilisation of the pure metal which retains the α-particles as helium within the metal lattice. A perfectly air tight apparatus is not necessary, as long as no air leaks in during the two hours duration of the experiment. The most suitable solvent for dissolving the metal completely and rapidly is a saturated solution of potassium cupric chloride. Measurement of the amount of helium per gram of metal of samples from the same piece, at two separate times differing by about 2 months when employing a 20 gm. sample, would enable us to calculate the disintegration constant of UI.

Our values for the disintegration constant was in agreement with that of Kovarik and Adams.

--- CHAPTER 4 ---

CHAPTER 4.

THE CHEMICAL COMPOSITION OF THE STRATOSPHERE.

1. INTRODUCTION.

Analyses of air in the troposphere over various geographical regions of the earth's surface have shown that the percentage composition is remarkedly constant. Water vapour in the air varies, naturally, according to geographical position, weather and height, and consequently tables of composition usually refer to dry air.

TABLE I.

GAS	COMPOSITION (% by vol:)	DENSITY (air = 1.000)
NITROGEN	78.99	0.9670
OXYGEN	20.95	1.1053
ARGON	0.93	1.377
CARBON DIOXIDE	0.03	1.529
NEON	1.82×10^{-3}	0.6963
HELIUM	5.24×10^{-4}	0.1381
KRYPTON	1×10^{-4}	2.868
XENON	8×10^{-6}	4.525
OZONE '	1×10^{-6}	1.624
RADON ''	6×10^{-18}	
HYDROGEN	1×10^{-4}	

' Variable -- increasing with height.

'' Variable -- decreasing with height.

The atmosphere up to some unknown height is constantly in a state of turbulence, which maintains a constant composition of the atmosphere, there being no time for the lighter constituents to separate out by diffusive segregation. The density of the air in the troposphere will therefore vary exponentially with altitude and will also vary with the temperature, in accordance with the following equation :

$$\rho = \rho_o \, e^{-h/H}.$$

where ρ is the density at any level h

ρ_o is the density at ground level.

and H is a quantity, having the dimensions of a length, and defined by RT/m_og where m_o is the mean molecular weight of air.

If the troposphere is uniform in temperature and composition, and g is to all intents and purposes constant, then H is constant. It is sometimes referred to as the "height of homogeneous atmosphere", because the total mass of the atmosphere, per vertical column of unit cross-section is $\int_0^\infty \rho \, dh$ or $\rho_o H$, the same as for an atmosphere of uniform density and total height H (C2).

Now should turbulence cease to exist, and the air remain perfectly still, the lighter constituents will have an upward velocity of diffusion relative to the heavier ones. This velocity, in a mixture of given composition, is uniformly proportional to the density and therefore should increase with altitude. The constituents will distribute according to Dalton's Law and the following equation will hold good: -

$$\rho x = \rho_o \, e^{-h/Hx}$$

where ρx is the density of constituent x at any height h.

and $Hx = RT/m_xg$ (m_x = molecular weight of x) (M2).

Maris and Epstein (M1), have calculated the rate of diffusive segregation of various constituents at various heights assuming the air to be thoroughly mixed and then left undistured for a certain length of time. Equilibrium will set in more rapidly at high levels where the pressure is low. The following table shows their results :-

TABLE II.

HEIGHT (km)	He	A	$CO2$
200	2 min.	12 min.	8 min.
180	26 min.	2.3 hrs.	1.6 hrs.
160	4.8 hrs.	25 hrs.	17 hrs.
140	2.8 days	14.8 days	10.4 days
120	34 days	180 days	130 days.
100	1.2 years	6.4 years	4.5 years.

(for 50% diffusive segregation).

Assuming, therefore, that the disturbance causing mixing of the constituents occurs periodically, from the above data, and knowing the period of the disturbance, we can estimate an altitude where the percentage of diffusive segregation is large during the period of the disturbance. Consequently, should the disturbance be due to the, say, change in temperature between night and day, we can say that there will be approximately ten hours rest in the atmosphere. This corresponds to a height of 150 km., above which height more than 50% of the helium will segregate from the remaining gases.

Observations on meteor trials at heights of 70 km. and also on noctilucent clouds between 80 km. and 100 km. show that these regions are subject to strong winds. From Maris and Epstein's figures we must expect that diffusive segregation cannot occur below 100 km.

As we proceed higher in the stratosphere this diffusive power must slowly preponderate and the composition of the air will slowly change, giving a greater percentage of the lighter gases. Evidence of spectroscopic data of the Aurora, however, show no trace of either helium or hydrogen but mainly oxygen and nitrogen in atomic and molecular form. (A recent publication by Herman, however, suggests that a number of bands in the spectrum of the night sky may equally well be attributed to a superimposition of Helium on a Nitrogen spectrum as to a metastable Nitrogen spectrum (H1). But this fact does not definitely prove that helium and hydrogen are not present in the upper atmosphere. It is not known whether or not helium or hydrogen are expected to emit light under the conditions of Auroral excitation. We could, on this basis, say that mixing overcomes diffusion throughout the stratosphere as well as the atmosphere and that helium exists in the same proportion throughout; or, on the other hand, due to the high temperatures which exist in the upper atmosphere, thermal diffusion of helium atoms will be so great, that the light gas will escape altogether from the earth's surface. At certain times of the year this temperature rises to as much as $1000^{\circ}A$.

The hydrogen content of the troposphere is very small, and in the stratosphere the possibility of the molecules dissociating into atoms which have thermal velocities about one and a half times as great as hydrogen molecules, exists with an even greater reason for loss of hydrogen from the earth. (J1,C2). Helium is continually being evolved from rocks which are slowly being sedimented during the ages, and this fact would account for the much greater proportion of helium to hydrogen in the troposphere.

In air at ground level there are 1.4×10^{14} atoms of helium per c.c. and at the base of the stratosphere (i.e. 10 km. high) 3×10^{3} atoms; the total column would therefore contain 1×10^{20} molecules per sq. cm. On an average, the number of α-particles produced per second per gram of igneous rock on the earth's surface is 1.2 If we take the age of the earth as 3×10^{9} years then the total number produced in geological time per gram of rock is $3 \times 10^{9} \times 365 \times 24 \times 3600 \times 12$, which is approximately 4×10^{16} atoms of helium. From the amount of sodium which has sedimented during the ages, knowing that the average content of sodium in rocks is about 2.8%, it has been estimated that 8.3×10^{23} gram rock have been washed away. The area of the earth's surface is 4×10^{18} sq. cm. and 8.3×10^{23} gram is equivalent to 1.6×10^{5} gram per sq. cm., which would release 6×10^{21} helium atoms into the atmosphere per sq. cm. of the earth's surface. But only 0.1×10^{21} atoms per sq. cm. remain, consequently more than 98% of the helium produced in geological time has disappeared from the earth's surface.

Conclusive evidence of the existence of an excessive proportion of helium can only, at present, however, be proved by gas analysis of air samples taken from the stratosphere (L1).

Both oxygen and helium contents have been measured in samples collected by manned and unmanned balloons up to a height of 29 km. Figures indicate no deviation in the percentage composition of either gas up to 20 km. After this level, there is an indication of an increase of helium and a corresponding decrease of oxygen. These variations are rather spasmodic with no definite increase with altitude. Though the analysis of the air sample taken at 21 km. has a surplus of 7% helium, one of the analyses at 23.5 km. only indicates a surplus of 0.5%. It is quite possible that the air sample became contaminated with excess helium in some way. The same may be said about the oxygen analysis. As will be seen later, oxygen can very easily be lost during the sealing of the sample bottles (R4). To all intents and purposes there is sufficient turbulence up to 30 km. to prevent any appreciable diffusive segregation occurring. Though we cannot expect turbulence to cease altogether, we would expect diffusion to overcome mixing uniformly and therefore show a steady increase in the surplus of helium. It can be shown mathematically, that, should turbulence cease altogether, the proportion of helium would increase by 14 per cent per km. height (C3).

Before anything of a definite nature can be remarked about this surplus of helium, it will be necessary to obtain air samples from a much greater altitude. Since 30 km. is practically the limit for unmanned balloons, we must turn to other modes of sampling. During the past three years a team of scientific workers in the Department of Aeronautical Engineering at the University of Michigan, U.S.A., have developed ingenious methods of sampling stratosphere air in metal bottles during tests with V2 rockets. A number of successful flights have been carried out, and thanks to Professor M.H. Nichols and Dr. D.W. Higelberger of the University of Michigan, and to Dr. Michael Ference of the U.S. Signal Corps, and the permission of the Meteorolical Branch of the U.S. Signal Corps, we have been able to analyse one or two samples taken during the flights.

A paper has already been published in "Nature" giving the results of our first analyses. (C1).

TABLE III.

Helium and Oxygen contents of the Stratesphere.

Ht. in Km.	Helium		Oxygen.	
	10^{-4}% by vol.	Varaition (% He)	% Vol.	Variation (% O_2)
0	5.240	0	20.945 20.92_3	0 0
9-17			20.92_4	0
14.5			20.89_3	-0.14
16.5	5.27	0.5		
18.0	5.26	0.4		
18.5	5.28	0.7	20.95_5 20.84_3	0 -0.38
19.0	5.27	0.5	20.87_3	-0.38
21.0	6.64	7.0		

Table III continued.

Ht. in Km.	Helium 10^{-4}% by vol.	Variation (% He)	Oxygen. % Vol.	Variation ($\%O_2$)
21.5			20.895_2	-0.24
22.0	(5.45 (5.34	(4.1 (2.0	20.57_3	
22.5	(5.51 (5.34	(5.1 (1.9		
23.5	(5.46 (5.27	(4.2 (0.5		
24.0			24.74_3	-0.86
25.0	5.35	2.1		
28 - 29			20.39_3	-2.5

(P6, G3).

2. METHOD.

(a) COLLECTION AND PREPARATION OF AIR SAMPLES.

When air samples were collected during the flights of unmanned balloons, small evacuated flasks of some 500 cc. capacity were employed. At the required altitude, or when the balloon burst, the opening of a small parachute used to convey the scientific instruments back to earth, automatically broke a glass capillary admitting air into the flask. After a few seconds, a timing device switched on a heating coil encircling the glass capillary. The heat melted some picein wax which sealed the capillary. Due to the excessive heat generated by the V2 rockets passing through the atmosphere, such a device became unsuitable at higher altitudes.

In V2 flights, metal bottles were employed, substantial enough to withstand the sudden shock of returning to terra firma without the assistance of parachutes. These metal bottles of some 500 cu. in. capacity were thoroughly tested beforehand, for mechanical shock by dropping on to a concrete floor from 100 ft. and for leakage, by first baking under vacuo at 150°C for 24 hours, leaving under vacuum for a few days and then testing for leakage of air by means of a hot wire gauge installed in each bottle.

One end of the bottle was sealed with a glass teat and a scratch mark made around it. The teat itself was protected by a metal cap screwed to the bottle, and containing a "mouse-trap" and "rat-trap" assembly. At some stage during the flight of the V2, usually during the free climb, a timing mechanism operated a relay which passed an electric current through a fuse wire holding a small metal bar against a spring ("mouse-trap"). When the fuse burned through, the bar was released and forced suddenly by the spring against the teat. This was severed at the scratch mark and allowed air into the bottle via an inlet manifold. The latter had an inlet port protuding a few inches outside the V2, and an exhaust, so that the whole was continually flushed with air as the V2 proceeded upwards.

A few seconds after the "mouse-trap" operated, a 400-cycle power supply released the rat-trap assembly, which squeezed tight a small copper tube between the glass tube and the bottle itself. The copper was tinned inside, and sufficient heat was generated to securely solder the copper tube and produce an air tight seal.

Both the "mouse-trap" and "rat-trap" mechanisms were discarded later and replaced by pyrotechnic openers and sealers. Squibs fired by the timing circuit, ignited a black gun-powder, which created enough pressure to drive down a small hammer to either break a glass seal or clamp shut the copper tube for sealing. Sufficient heat was generated by the powder to carry out the soldering mentioned above.

On recovery of the bottles, a sample extractor was coupled to the bottle, and this assembly evacuated. Inside this extractor was a punch which could be screwed into the copper diaphragm (at the opposite end of the bottle from the opening and sealing mechanism), puncturing it and releasing the air into the sampling apparatus. A pressure reading was taken to check that the sample had been taken at the correct altitude, and that no leak had occurred. The sample was then pumped by Toepler pumps into 50 cc. lime glass flasks equipped with septa and therefore suitable for fixing directly to our apparatus.

(b) METHOD OF ANALYSIS.

The method employed in analysing the samples for helium and neon was similar in many respects to that employed by Glueckauf (G3), and entailed the removal of oxygen by a heated copper spiral from a known volume of air, and measuring the absolute volumes of helium and neon present, by the Helium Apparatus. A separate apparatus employing heated calcium was used to measure the volume of argon.

The lime glass flasks received from America, were sealed to the apparatus at A, and a small steel ball removed from the side-tube indicated in the diagram (Fig. 10), by means of a magnet, and allowed to drop suddenly, broke the septa and released the air samples. U-tube B was cooled with liquid oxygen to trap the water vapour and carbon dioxide, if any, before the gas reached the Toepler pump. Here all the gas could be concentrated in bulb C by Toeplering about a dozen times. A fraction of the samples was introduced into D, the reaction chamber, where oxygen was removed with the heated spiral, leaving nitrogen, argon, neon and helium. Pressure readings were taken with the mercury meniscus touching the glass tip shown in the diagram.

Reduction of the spiral was accomplished by introducing hydrogen or coal-gas via the left arm of the 3-way stop-cock. Passing a small current

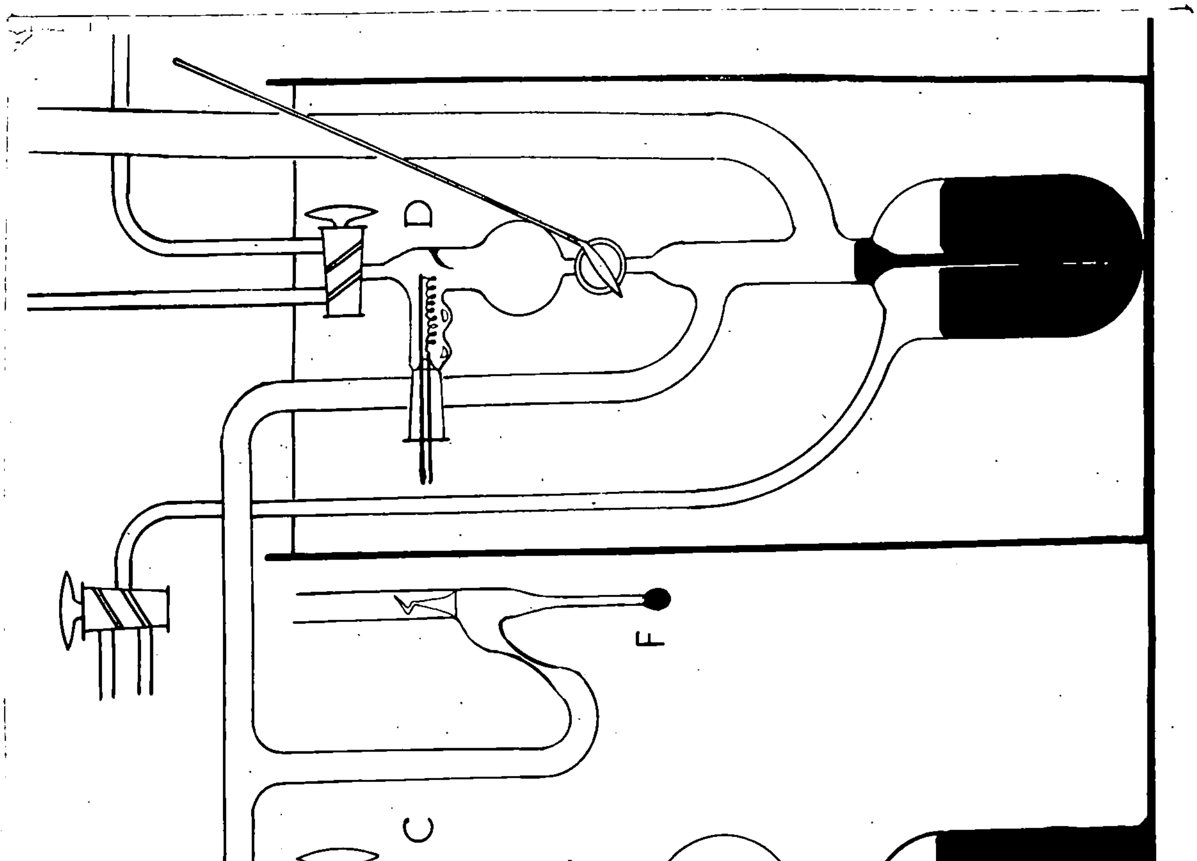


Fig. 10.

so that the copper just glowed for two minutes was long enough for the reduction. The two pieces of potassium hydroxide were there to make sure the air samples was dry and to absorb any water vapour produced should hydrogen have been present in the sample.

It was necessary to determine the volume of the reaction chamber D in situ, A few ccs. of ordinary air in a flask similar to A were employed, the septa broken as above, carbon dioxide and water vapour removed, and the whole of the sample Toeplered into C whose volume had been determined prior to installation. The pressure of this gas was measured with a kathetometer using the side-tube leading from the U-tube as the evacuated limb.

Let volume of C be V_1 and this pressure be P_1.

With the mercury raised beyond the vacuum tube of the reaction vessel, and just beyond G, the tap C was epened, so that the gas distributed into the side-tube to G. The mercury levels at C were adjusted again and another pressure reading taken --- P_2. By lowering the mercury at G a fraction of an inch, the gas expanded into D, and another pressure reading was taken --- P_3. Then the mercury was raised to the tip D, and this time a pressure reading taken at D.

Thus, if V_2 = volume of side-tube.

V_3 = volume of reaction chamber + bulb.

V_4 = volume of reaction chamber.

then,

$$P_1V_1 = P_2(V_1 + V_2) = P_3(V_1 + V_2 + V_3)$$

therefore

$$V_3 = P_1V_1(1/P_3 - 1/P_2).$$

Since only the fraction of gas occupying the reaction chamber and bulb was concentrated into the reaction chamber, then

$$P_3V_3 = P_4V_4$$

Therefore, $$\underline{\underline{V_4 = P_1V_1(P_2 - P_3) / P_2P_4.}}$$

When removing the oxygen from the sample, the gas was first allowed to partly expand into the bulb below the reaction chamber, A small current was passed through the copper until the latter was just visible in a darkened room, for two minutes, and then the gas allowed to cool before raising the mercury and taking a pressure reading. The process was repeated until the reading became constant. Thus the percentage of nitrogen plus argon was calculated.

Helium and neon were separated in the normal way by means of the fractionating column of the Helium Apparatus, and measured separately in the Pirani gauges.

A small percentage of the samples were adsorbed on F (fig. ~~10~~ 11) cooled in liquid oxygen. This was then sealed off and fixed to the Argon Apparatus.

Oxygen of this sample was determined by precisely the same method as above, using copper A, and then the nitrogen and argon transferred to the Calcium Furnace by adsorbing on charcoal B (fig. ~~10~~ 11). The calcium was vapourised and at once combined with the nitrogen to form a nitride. All that remained of the stratosphere air sample was argon and a negligible quantity of other rare gases. The volume of the argon was determined with the McLeod Gauge C.

2. EXPERIMENTAL.

(a) MEASUREMENT AND REMOVAL OF OXYGEN.

Oxygen, because of its ability to combine with most elements of the Periodic System, and the ease of adsorption by glass and most forms of grease, is not an element which can be analysed in small quantities with any high

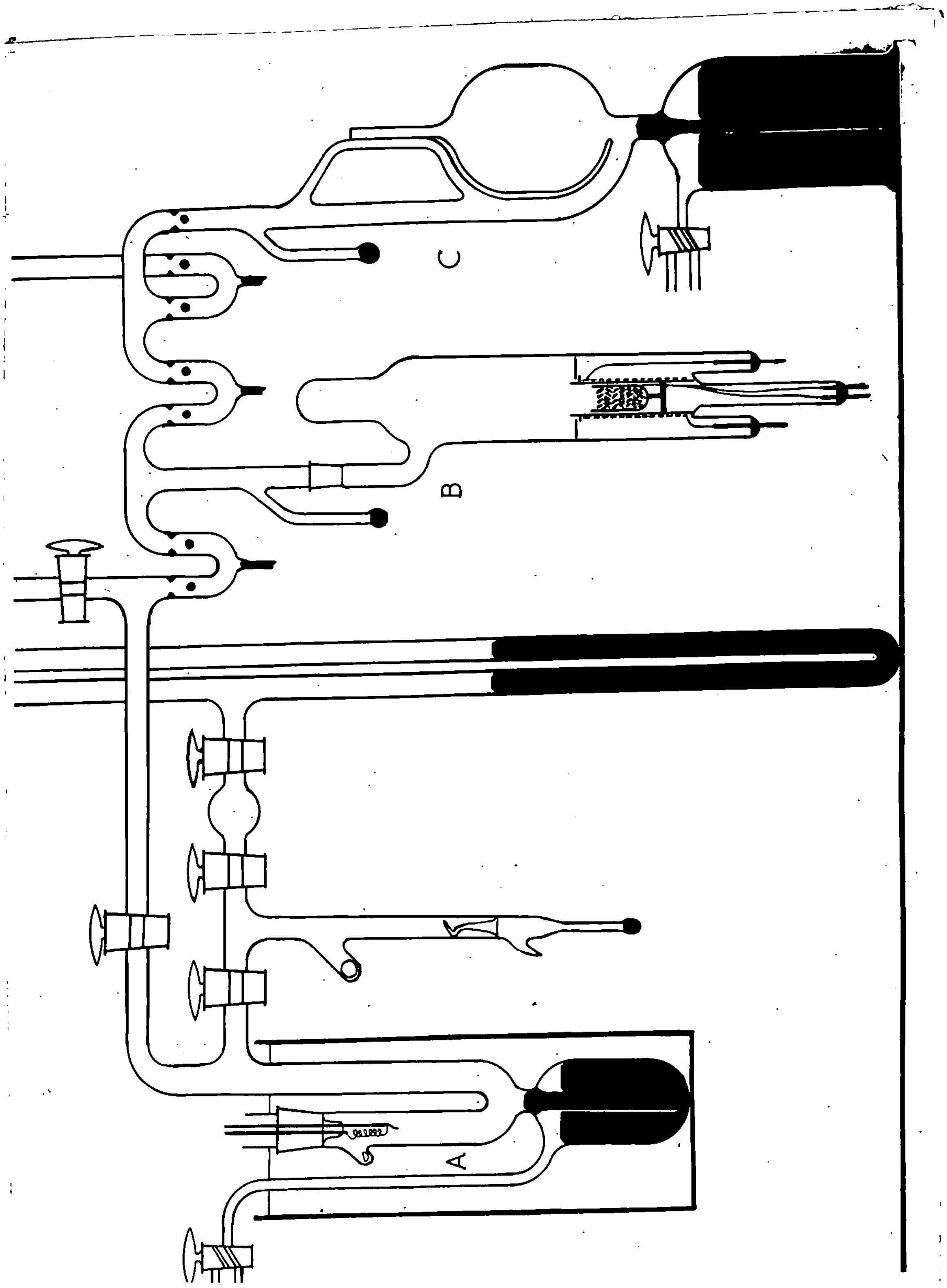


Fig. 11.

degree of accuracy. The usual method adopted for estimation in a dry gas, is by combination with heated copper wire, when the diminution in pressure of a known volume of gas is a measure of the oxygen present.

Though it may appear a simple operation to pass an electric current through a copper spiral suspended in the gas, and continue the process until the pressure becomes constant, it is not so easy to obtain very accurate results unless certain precautions are taken. Copper oxide, for instance, dissociates at high temperatures and evolves oxygem. It is therefore necessary to maintain a fairly low working temperature.

After a few experiments with air samples, we finally adopted the following procedure whenever introducing an ordinary air sample into the reaction chamber and determining the oxygen content : -

(1) The copper spiral was reduced with coal gas using approximately 5 ccs. at 1 cm. pressure. This was done by passing current through the copper, which quickly turned reddish in colour, and the heating continued for two minutes to complete the reduction. Any occluded hydrogen on the copper surface was removed by heating the copper with the reaction vessel open to the pumps for 5 to 10 minutes.

(2) When air was introduced through the stop-cock above D,(method adopted when a stratosphere air sample was already fixed at A-), the open arm of the stop-cock was always flushed out beforehand. (This also concerns the Helium measurements --- see later).

(3) Air was dried before introduction to avoid saturation of the potassium hydroxide pellets. (This also concerns helium and neon measurements.)

(4) The oxygen content was determined immediately after the air was introduced, because of the active state of the copper which is capable of removing a percentage of the oxygen even if left in contact with air for

periods over about one hour.

(5) Removal of the oxygen was accomplished with a glowing copper spiral, just visible in a practically darkened room. After two minutes oxidation the gas was allowed to cool and a pressure reading taken after five minutes. The heating was repeated until a constant reading was obtained. With skill it was possible to remove more than 99 per cent of the oxygen during the first heating and the remainder during the second.

As an indication of the ease of combination of oxygen, we analysed a sample of air which had first passed over some warm iron before being introduced into the reaction chamber. In actual fact, the vacuum pump of the Helium Apparatus was switched off and before the metal mercury diffusion pump had cooled down completely, the main vacuum line was quickly opened to the atmosphere. Part of this air was then used as the sample. Though the speed of passage over the heated metal was very rapid, more than 20 per cent of the oxygen had been removed from the sample!

<u>VOLUME OF REACTION CHAMBER.</u>

$P_1 = 6.784$ cms. at 23°C.

$P_2 = 3.254$ "

$P_3 = 2.050$ "

$P_4 = 11.343$ "

V_1 (standard) = 24.73 cc.

$$\text{Therefore,}\quad V_4 = P_1V_1\frac{(P_2-P_3)}{P_2P_4} = \underline{5.47\text{ cc.}}\ \text{capacity.}$$

Oxygen determinations carried out on sixteen samples are shown as follows, where the amount of oxygen is in per cent by volume of the total vokume of dry air taken

21.2, 20.2, 20.1, 20.5, 20.9, 21.3, 20.9, 20.9, 20.6, 20.4, 20.9, 20.6, 20.6, 20.3, 20.3, 20.8.

Mean with probable error = 20.7 ± 0.1 per cent.

(Glückauf's figure was 20.98 per cent.)

When the first two stratosphere samples were tested for oxygen, none was detected whatsoever. This can be explained when one studies the mechanism of sealing the stratosphere air samples in the metal bottles - tinned copper heated to a high temperature and retaining this high temperature for many minutes, when the heat of the bottle can only be lost by conduction and radiation and very little by convection at the reduced pressure. However it is rather remarkable that the oxygen should completely disappear from the sample, especially when it is already in the bottle before the heat is applied to the tinned copper. No other explanation could be found accounting for this phenomenon - oxygen must exist at this altitude certainly more than just a fraction of a per cent. In later samples, oxygen was detected and measured, but in no case was the percentage as much as in ordinary air.

Hydrogen was also tested for in the sample. An oxidised copper spiral was employed, but on heating in the stratosphere air samples, there was no noticeable decrease in pressure, indicating less than 0.05 per cent hydrogen.

(b) MEASUREMENT OF HELIUM AND NEON.

(1) HELIUM AND NEON DISTRIBUTION OF THE FRACTIONATION COLUMN.

The fractionation column has already been described in a previous section of this work.

During most of the experiments on stratosphere air analysis, liquid oxygen was used as the cooling agent for the charcoals of the column and the Pirani gauges. Oxygen boils at a constant temperature and does not become contaminated with other lowerboiling gases. The boiling point of hydrogen on the other hand, will gradually increase, due to the slow absorption of oxygen from the atmosphere. Contamination with oxygen, however, was not as large as expected, and it only became necessary to use a fresh supply every three days.

The disadvantage encountered when using liquid oxygen, was the poor separation of helium and neon. As much as six per cent of the neon was estimated to be liberated with the helium fraction and, unless conditions were exactly the same during each experiment this figure was found to alter. As a result of this, we eventually reverted to liquid nitrogen both on the column and for the gauges, and tested the temperature periodically with a vapour pressure thermometer. With this lower temperature a much better separation of the two inert gases was accomplished.

Though, theoretically, one should obtain the same proportion of gas in each operation of the fractionating column, the temperature being constant, the amount of charcoal in the U-tubes being always the same, and the volume of the bulb being constant, in practice, however, many conditions govern the proportions. Firstly, the level of the liquid oxygen or nitrogen in the Dewars - the charcoals must be constantly below the level of the liquid. Secondly, the time allowed for the gas to reach equilibrium between the adsorbent and the gas phase at each operation - after practice, it was found that a convenient time was 10 seconds. Thirdly, the room temperature - this was especially noticeable during calibration of the Piranis. The sensitivity seemed to increase linearly with room temperature. Perhaps this may have been due to having most of the Pirani space outside the Pirani Dewar, so that with increased temperature, the proportion of gas not cooled by liquid nitrogen would be decreased and consequently a large deflection would result.

The distribution was carried out by Toeplering pure helium or neon from the calibration part of the Helium Apparatus into the circulating apparatus, and from here introduced into the fractionation column in the usual way. Naturally the same dead space prior to the first charcoal was used in the distribution experiments and in the air analyses. Fractions of gas coming over after the 12th operation ~~was~~ measured individually. From the results, the best "dividing line" between helium and neon was estimated and the percentage of each gas at each side of this line. The column had been built originally with the correct amount of charcoal in each U-tube to give the separation after the 24th operation using liquid nitrogen. With liquid oxygen, 99.3 per cent of the helium came over in the first 25 operations together with 6 per cent of the neon. By lowering the Dewar after the appropriate number of operations, all the neon was liberated from the charcoals in the next 25 operations.

After it was discovered that even these figures were not constant and altered by as much as 3 per cent, we once more reverted to liquid nitrogen. With the latter 98.6 per cent helium came over in 30 operations and all the neon afterwards.

Before we attempted the analyses of the third and fourth stratosphere air samples, we decided to use the correct amount of charcoal in the column to give the best theoretical separation of helium and neon at the 24th operation using liquid nitrogen. (The amount of adsorbent had been changed when liquid oxygen had been used.) We were not successful in obtaining complete separation, finding that 1.5 per cent neon came over in the first 25 operations with the whole of the helium.

(2) Helium and Neon in the samples.

During the initial experiments with ordinary air, occasional experiments resulted in a "tailing" of the neon deflections, i.e. a large number of further operations were necessary before the whole of the neon was apparently removed. This was thought at first to be due to hydrogen, either evolved from stop-cock grease or from the copper spiral after reduction in coal gas. Re-heating the spiral would perhaps release the hydrogen again.

It was not for some weeks, that a minute crack was detected in one of the charcoal tubes of the fractionating column. This crack had escaped detection previously by the Tesla coil and a poor vacuum had not been apparent when the charcoals had been baked, no doubt due to the expansion of the glass and consequent closure of the crack. After the charcoals had been cooled with liquid oxygen, there had been no indication of a leak by a deflection of the galvanometer spot when a blank had been performed on the column. It was only when the Dewar cooling the first five charcoals had been lowered far enough, that the leak had commenced. Therefore instead of a complete liberation of the neon on the samples by the 50th operation, the deflections "tailed". Only when on one occasion the Dewar had been lowered further than usual and operations of the column begun almost immediately afterwards, and therefore before the glass had warmed up sufficiently to close the crack, was it noticed that the mercury in the bulb following the third charcoal became damp in appearance and the bulb was evacuated of mercury more rapidly than neighbouring bulbs.

The presence of any pyrex glass in the Helium Apparatus can be a very disturbing factor. For example, pyrex keys to soda glass stop-cocks have caused a great deal of trouble in the past. First indications of such became known when one or two experiments with ordinary air gave a helium deflection far in excess of the expected value, although the neon deflection was correct. The bore of the key in question had not been evacuated for a day or two, and consequently a fair proportion of helium had diffused through.

3. RESULTS.

(a) SPECIMEN CALCULATION.

Measurement of Oxygen.

P_1 = 7.975 cms. at 18.0°C.

P_2 (after removal of O_2 with Cu) = 6.318 cms. at 18.0°C

$$\text{Therefore } \frac{N_2 + A}{\text{Total Air}} = \underline{79.2\%}.$$

Helium and Neon.

He deflection (13 - 25 ops.) = 30.97 cms.

Ne deflection (26 - 50 ops.) = 54.91 cms.

Now a negligible percentage of helium comes over after the 25th operation, but 3.1 per cent of the total neon comes over before the 25th operation.

$$\text{Therefore, total Ne deflection} = 54.91 \times 100/96.9 = \underline{56.7 \text{ cms.}}$$

$$\text{Therefore, total He deflection} = 30.97 - 3.1\% \text{ of } 56.7 = \underline{29.17 \text{ cms.}}$$

Calibration of Pirani gauge.

9.75×10^{-8}cc. per 1 cm. deflection for Helium.

1.72×10^{-7}cc. per 1 cm. deflection for Neon.

Volume of Reaction Chamber == 5.48 cc.

$$\text{Therefore, Volume of } N_2 + A = \frac{5.48 \times 6.318 \times 273}{76 \times 291} \text{ cc. N.T.P.}$$

$$= 0.426 \text{ cc. N.T.P.}$$

$$\text{Therefore, } \frac{He}{N_2 + A} = \frac{29.17 \times 9.75 \times 10^{-8}}{0.426} = \underline{6.65 \text{ ppm.}}$$

$$\frac{Ne}{N_2 + A} = \frac{56.7 \times 1.72 \times 10^{-7}}{0.426} = \underline{22.9 \text{ ppm.}}$$

$$\text{or } \frac{He}{\text{Standard Air}} = \frac{29.17 \times 9.75 \times 10^{-8}}{0.426 \times \frac{100}{792}} = 5.29 \text{ ppm.}$$

$$\frac{Ne}{\text{Standard Air}} = \frac{56.1 \times 1.72 \times 10^{-7}}{0.426 \times \frac{100}{79.2}} = \underline{18.0 \text{ ppm.}}$$

When galvanometer scale corrections were applied, the following was the method of calculation:-

Measurement of Oxygen.

P_1 = 3.590 cms. at 18.4°C.

P_2 = 2.850 cms. " "

Therefore, $$\frac{N_2 + A}{\text{Total Air}} = \frac{2.850}{3.590} \times 100 = \underline{79.4\%.}$$

$$\text{Volume of } N_2 + A = \frac{12.10 \times 2.850 \times 273}{76 \times 291.4} = 0.4232 \text{ cc. NTP.}$$

Helium Calibration

P = 2.203 cms. at 20.7 C

$V = 87.04 \times 2.203 \times (1 - .0034 (20.7-20) \times 10^{-8}$ cc.

$= \underline{1.914 \times 10^{-7} \text{ cc.}}$

Deflections.

(1) 12.65 between 44 and 31 of scale

Scale Correction = -0.28

True Deflection = 12.37 cms.

(2) 12.64 between 45 and 32 of scale

Scale Correction = -0.35

True Deflection = 12.29 cms.

(3) 12.60 between 45 and 32 of scale.

Scale Correction = -0.35.

True Deflection = 12.25 cms.

Mean Deflection = 12.30 cms.

Since volume of the calibration apparatus is approximately 400 cc., and volume of the calibration cup is approximately 1 cc. therefore in four calibrations, about 1 per cent of the calibration gas has been used. To estimate the correct deflection after three calibrations we must add 1/4% to the mean.

Therefore, correct calibration deflection

$$= 12.30 + 0.03 = 12.33 \text{ cms.}$$

Therefore, Helium Sensitivity

$$= \frac{1.914}{12.33} = \underline{1.554 \times 10^{-7} \text{ cc/cm.}}$$

Neon Calibration

$P = 5.125$ cm. at 19.8°C.

$V = 87.04 \times 5.125 \times [1-0.0034(-0.2)] \times 10^{-8}$ cc.

$= \underline{4.46 \times 10^{-6} \text{ cc.}}$

Deflections.

(1) 13.50 between 43 and 29 of scale.

Scale Correction = - 0.21

True Deflection = 13.29 cms.

(2) 13.62 between 43 and 29 of scale.

Scale Correction = -0.21

True Deflection = 13.41 cms.

(3) 13.56 between 41 and 27 of scale.

Scale Correction = -0.08

True Deflection = 13.48 cms.

Mean = 13.39 + $\frac{1}{4}$% = 13.45 cms.

Therefore Neon Sensitivity

$$= \frac{4.46 \times 10^{-6}}{13.45} = \underline{3.320 \times 10^{-7} \text{ cc/cm.}}$$

Helium and Neon from Air.

Operations 13-25 -- 18.02 between 45 and 26 of scale

Scale Correction = -0.27

True Deflection = $\underline{17.75 \text{ cms.}}$

Operations 26-35 — 26.11 between 45 and 19 of scale

Scale Correction = -0.13

True Deflection = 25.98 cms.

Operations 36-50 -- 2.92 between 42 and 39 of scale

Scale Correction = -0.11

True Deflection = 2.82 cms.

Now 1.5% of the Neon comes over before the 25th operation. Therefore

$$\text{total Neon} = \frac{25.98 \times 2.82}{0.985} = \underline{29.24 \text{ cms.}}$$

Therefore, total Helium = 17.75 - 0.44 = 17.31 cms.

$$\text{Therefore, } \frac{He}{N_2 + A} = \frac{17.31 \times 1.554 \times 10^{-7}}{0.4232}$$

$$= \underline{6.355 \text{ p.p.m.}}$$

$$\frac{Ne}{N_2 + A} = \frac{29.24 \times 3.320 \times 10^{-7}}{0.4232}$$

$$= \underline{22.42 \text{ p.p.m.}}$$

$$\text{or } \frac{He}{\text{Standard Air}} = 6.355 \times \frac{79.4}{100}$$

$$= \underline{5.046 \text{ p.p.m.}}$$

$$\frac{Ne}{\text{Standard Air}} = 22.42 \times \frac{79.4}{100}$$

$$= \underline{18.21 \text{ p.p.m.}}$$

(b) TABLE OF RESULTS.

(1) Experiments were carried out before the galvanometer scale error was discovered, and naturally with results whose individual readings varied greatly. They do however indicate that the helium and neon contents of the stratosphere at 70 km. differed very little from ordinary air.

HELIUM (ppm to standard dry air)	NEON (ppm)	ARGON (per cent of Standard dry air.)
Ground Air.		
5.37	18.9	0.915
5.23	18.2	0.905
5.35	18.6	0.915
5.42	18.2	
5.14	18.6	
5.20	17.5	
4.94	18.5	
5.25	18.2	
5.10	18.2	
5.25	18.1	
4.93	17.4	
5.39	18.1	
5.42	17.5	
5.03	17.9	
Mean + probable error		
5.22 ± 0.03	18.1 ± 0.08	0.912 ± 0.003
Stratosphere Air 1 B		
4.80	17.7	
4.92	18.3	0.925
Mean		
4.86 ± 0.04	18.0 ± 0.25	0.925
Stratosphere Air 3 B		
4.95	17.5	0.910
5.03	17.9	0.900
5.34	18.4	0.910
Mean		
5.11 ± 0.10	17.9 ± 0.15	0.907 ± 0.003

(O_2 less than 0.5%.)

(2) With a greatly improved apparatus, more accurate column distribution and a scale correction for the galvanometer scale, the following results were obtained :-

HELIUM (ppm)	NEON (ppm)	ARGON.
Ground Air.		
5.046	18.27	0.915
4.985	18.06	0.918
5.083	17.90	0.913
5.007	18.00	
5.077	18.15	
4.979	18.00	
5.078		
Mean		
5.026 ± 0.014	18.06 ± 0.05	0.915 ± .002
Stratosphere Air 15 B		
5.019	17.94	
5.052	18.07	
5.052		
Mean		
5.041 ± 0.009	18.01 ± 0.05	
	(O_2 = 3.25%).	
Stratosphere Air 16 A.		
4.950	17.85	0.911
4.948	17.64	0.910
4.966	17.58	0.916
Mean		
4.847 ± 0.005	17.75 ± 0.06	0.912 ± .002
	(O_2 = 16.27 per cent).	

(c) DISCUSSION.

In our first series of determinations, there were a sufficient number of analyses to give a fairly reliable result for the percentage of constituents of ordinary air, taking into consideration the mean probable error. Unfortunately, due to possible changes in the distribution of the column using liquid oxygen and the still greater source of error not known when the results were obtained, the lack of linearity of the galvanometer, the individual results were far from satisfactory. Due to the smallness of the samples supplied and the fact that part of these samples had to be removed for the argon analysis, more than three analyses each could not be attempted.

However, the results were sufficient to indicate the lack of any diffusive segregation; to all intents and purposes stratosphere air at 70 km has the same chemical composition as troposphere air. If diffusive segregation has occurred after 20 km., this is a peculiarity to that part of the stratosphere, and turbulence predominates again at higher altitudes.

Unfortunately, after these results were obtained, word was received from America, that the samples may in actual fact have been just ordinary ground air. The latter may have been trapped during the flight of the rocket, and perhaps, due to the great speed of the rocket, could not escape completely. Consequently on opening of the bottles during the free climb of the V2, instead of stratosphere air rushing in through the inlet manifold, ordinary ground air forming a film around the rocket, entered. It must be remembered, however, that calculations on the pressure of the samples taken corresponded with air taken at 70 km. It is most probable that, if the air flushed into the bottles had been ordinary air, the pressure reading would have been higher than expected.

Alterations were accordingly carried out so that in future flights, there would be no likelihood of this possible contamination. The air bottles were fitted into the nose of the V2, in a special compartment which could be sealed off and evacuated prior to the flight. The chance of air from the rear compartments forming a film of air around the nose of the rocket was very remote unless the mach angle became greater than 90°, when the samples were taken. These samples, which we received and analysed within a month of the launching, were definitely of stratosphere origin.

Before the second series of analyses, we had carried out the galvanometer scale calibration and produced a table giving the correction to be applied to any deflection. We were pleased to obtain such consistent results with a probable error between 5 and 20 times smaller than the corresponding results with our first effects. We are satisfied that stratosphere air at least at altitude 50 km. is the same as ground air.

Up to the date of writing this thesis, we have found no explanation for the absolute difference between our helium ratio and that of Glueckauf, namely 5.239 ppm. The capacity of our reaction chamber was rechecked, the distribution of the column remained constant and if the helium for calibration had been contaminated the apparent helium content would have been greater not smaller. If the distribution of the column had changed during the course of the experiments, one would expect inconsistent results, whereas, in actual fact, the results indicated were determined intermittently during the three weeks duration of the analyses. In any case, had the distribution altered just after the actual measurement and prior to measurement of the last series of results, and remained constant during this period, so that the ratio of neon to helium became 3.47 : 1, then the neon would accordingly be reduced. To compensate for this the reaction vessel volume would have to alter by as much as 2 per cent, to bring the figures for helium and neon up to those obtained by Glueckauf. We measured this reaction volume three times and obtained a mean result with error less than ½%. Thus we have no explanation for this discrepancy.

But the absolute error does not invalidate out statement that stratosphere air is to all intents and purposes of the same chemical compositio as ground air. An occasional deficit of helium can be ascribed to the condition of the glass apparatus employed for extracting the samples from the bottles. The troubles encountered during experiments with helium using glass apparatus are well known, and glass dissolves helium appreciably. Consequently if glass freshly heated is used shortly afterwards as a reservoir for air samples, helium will be dissolved to make up the deficit. Hence a possible reason for the deficit in samples 16A, a sample taken during the same flight as 15B.

The method of analysis could be improved, somewhat, if a more suitable metal than copper were used to remove oxygen. The metal would have to be capable of removing all the oxygen and also retain the gas when strongly heated. A magnesium or zinc ribbon flashed in the air sample would do the trick, but this involves removal of the wire assembly after each experiment, and unnecessary delay in obtaining a really dry reaction chamber again. The wet method is not suitable because of the small quantities employed and it is doubtful that oxygen would be completely removed.

As long as the method of sealing the metal bottles is employed, a fair portion of the oxygen will disappear. It would be best to have a double cap consisting of a Al or Cu tube connected to another Cu tube via a heat insulator. After entry of the stratosphere air, the Al or Cu tube nearest to the bottle could be clamped shut with a hammer mechanism, and a fraction of a second later the outer Cu tube clamped shut and soldered. With such a cap the leak of air through the inner closed tube would be so slow that the tinned copper would have completely cooled and so be ineffective in removing oxygen.

Argon being a heavier gas than either oxygen or nitrogen, any indication of diffusive segregation will be more apparent if the helium/argon ratio is employed. There is no necessity to remove the oxygen unless absolute quantities are required. We found no deviation of the percentage of argon in the stratosphere air to that in ordinary air.

4. CONCLUSION.

Analyses of stratosphere air collected by V2 rockets fired in America to altitudes of 70 and 50 kms. have indicated a negligible difference in the composition compared with ground air, as far as nitrogen, argon, neon and helium are concerned. Oxygen has been partly removed in each case due to the mechanism of closing the sample bottles. Absolute values for all gases except helium, in both ground air and stratosphere air agreed with the values determined by Glueckauf for ground air. The mean figure for helium in our first series of results agreed with Glueckauf, but in our more accurate second series, the mean was about four per cent low, although the neon determination agreed. No explanation, to date, has been found to account for this discrepancy.

Three analyses plus an argon determination could be performed with as little as 1.5 cc. NTP of sample.

From our results we have reason to believe that diffusive segregation does not overcome turbulence in the stratosphere below 50 km. at least. Helium is not a reliable gas for indicating accurate differences in composition of air despite the low density and inactivity if glass vessels are used. A more suitable gas for the purpose is neon.

CHAPTER 5.

THE MEASUREMENT OF HELIUM IN METEORITES.

1. INTRODUCTION.

It is now of general belief, though not definitely proved, that meteorites which strike the Earth, belong to our Solar System. They afford the only means available at present, of analysis and age determinations of extra-terrestrial matter, the pioneer work of which has been extensively conducted by Paneth and his collaborators since 1928. (P5, A1)

Up to 1942, a considerable number of meteorites were analysed for the volume of helium occluded and for the amount of radioactive material present. Quantities up to 20 gm. were dissolved in a suitable solvent such as potassium cupric chloride or hydrochloric acid, the hydrogen removed by burning with oxygen and the helium measured by the Helium Apparatus. After dissolution the radium and thorium X present were precipitated together with barium as sulphates, the latter converted into chlorides and the thoron and radon evolved from the chloride solutions measured in an ionization chamber connected with an electrometer valve. The thoron, because of its short half-life, was measured immediately after preparation of the solution in a stream of nitrogen, whereas the radon was allowed to accumulate before measurement.

Controlled experiments showed that it was possible to measure quantities of radium of the order of 1 x 10^{-13} gm. (corresponding to an equilibrium amount of 3 x 10^{-7} gm. uranium) and of thorium salts of the order of 1 x 10^{-6} gm, to an accuracy of 10 per cent, Since all meteorites contain similar amounts of uranium, usually about 1 x 10^{-8} gm/gm., 30 gm. meteorite will be necessary to measure to the above accuracy. The limits of error in the measurement of the helium were negligible, but were high with the thorium. However, it was most probable that age values were not more than 1,000 million years out in the case of the highest ages. This is not a lot when one considers that ages estimated were as high as 7,000 million years, a value which is twice as high as the reputed age of the Earth.

At the time of publication of the results obtained on meteorite analysis, an upper limit to the age of the Solar System had hot been estimated. Consequently, Paneth, though he mentioned how one must be sceptical about age determinations obtained by the Helium method, because of the inability of scientists to explain the "excess helium" in the minerals beryl and magnetite, concluded that the age of the Solar system could hot be less than 7000 millions years. This is considerably higher than the age of rocks of the Earth, which have been determined by a more reliable age method - the Lead Method.

It is now geologically established that the age of the oldest rocks is of the order of 3500 million years. If we assumed that this figure is representative for the age of the Solar system we must turn to some hypothesis to account for the "excess helium" present in meteorites. One hypothesis was put forward by Bauer in 1947 (B1).

Bauer plotted the helium contents of meteorites obtained by Paneth against the logarithm of the masses and concluded that smallest meteorites have the largest helium contents and vice versa. This effect indicates that the helium contents are related to the pre-atmospheric masses and actually opposite to what we would expect if there had been an appreciable leakage of helium. Bauer states that this phenomenon would be expected if cosmic radiation was the source of the helium. Observations show that cosmic rays give rise to nuclear disruptions, and that α-particles are among the disintegration products. From published data he adopted the following:-

(1) $n = 1$ = average number of α-particles produced per disruption.

(2) $L = 150$ gm./cm^2 = mass in which on an average one cosmic ray particle will give one disruption.

(3) $J = 1.5$ = number of primary cosmic ray particles crossing the unit area per second.

Thus, helium production is $N = \frac{nJ}{L} = 10^{-2}$ αs/sec/gm. meteoroid.

Consequently for a very small meterorite (negligible absorption of cosmic rays) the disruption process will produce the maximum observed helium content (4×10^{-5} cc./gm.) in 3.4×10^9 years - i.e. within a time equal to the present assigned age of the Solar System.

Since in the atmosphere we never observe primary cosmic rays with energies less than 3 BEV, and if this can be attributed to the sun's magnetic field, it is possible that cosmic rays at solar distances about 3 astronomical units (an acceptable distance if meteorites come from a disrupted planet between Mars and Jupiter) will produce α-particles. On this assumption, helium production in meteorites may be as much as 100 times the figure quoted above.

In his second paper, Bauer (B2) calculates the radial distribution of helium produced by cosmic rays, assuming it to be proportional to the cosmic ray intensity. He deduced a formula:-

$$\frac{N(r)}{N_0} = \frac{1}{4\pi}\int e^{-d/D}\,d\omega = \frac{1}{4r}\int_{R-r}^{R+r} e^{-d/D}\,dd + \frac{R^2-r^2}{4r}\int_{R-r}^{R+r} \frac{e^{-d/D}}{d^2}\,dd$$

where N_0 = primary cosmic ray flux through a sphere of cross section 1 cm^2 in free space.

$N(r)$ = flux at a point P, r cms. from the centre of a (iron) meteorite, radius Rm density = 7.8gm/cc.

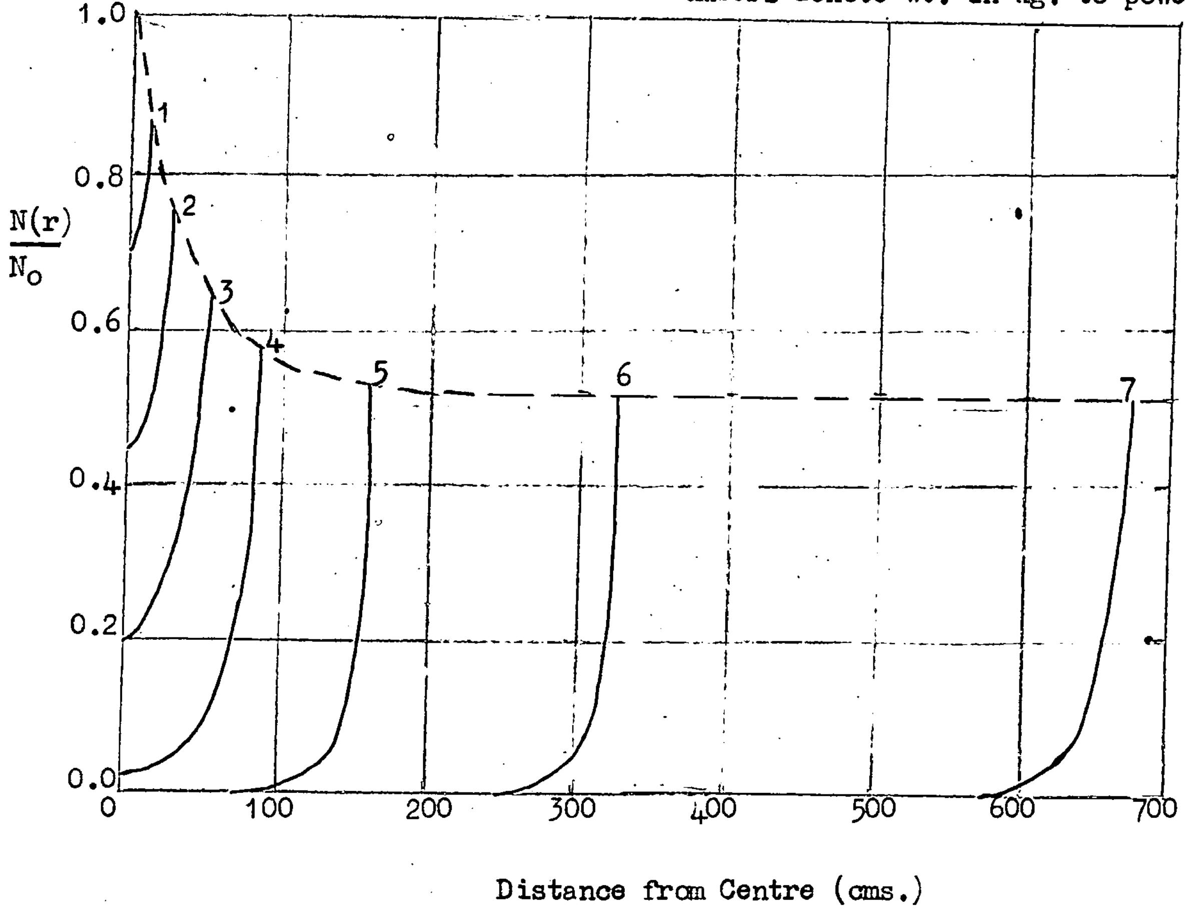
d = distance from point P to any point on the surface of the sphere.

D = distance in which on average one primary particle produced one nuclear disruption (= 19.2 for iron).

From this he calculated $N(r)/N_o$ as a function of r, for meteorites of masses 10^1, 10^2, 10^3 ---- kg.

Bauer plotted such calculated values against the distance from the centre of the meteorite and obtained the following graph.

Numbers denote wt. in kg. to power 10.



From this graph, it is obvious that cosmic ray helium at the edge of metorites larger than about 10^5 kg. can be little over half that in an extremely small meteorite, due to the large mass of the meteorite shielding any edge from half the cosmic rays of free space. There will also be large radial variations in the helium content of all meteorites except at points more than 80 cms. from the edge. This is only the case with meteorites of greater mass than 10^4 kg. In very large meteorites the helium produced at the centre from cosmic rays will naturally be very minute.

Bauer, in the same paper, calculated the helium contents per gram. at the edge and at the centre of meteorite of different masses, assuming that some of the outer crusts of the original meteoroids were lost in the atmosphere. He assumed that cosmic radiation produced 4×10^{-5} cc./gm. at the centre of a meteorite of mass 10 kg., and that all meteoroids have been irradiated for the same length of time. Actual values obtained by Paneth, when plotted on the same graph appear near the theoretical curves.

He finally states that if 4×10^{-5} cc./gm. is actually produced in small meteorites by cosmic rays, than the process is sufficient to account for all meteoritic helium.

Paper three (B3), summarises the evidence that cosmic rays account for many of the phenomena associated with the varying helium contents of meteorites. Bauer quotes the case of the Bethany meteorites which appear to be identical in composition, though containing varying amounts of helium. (Goamus 0.15 x 10^{-6} cc/gm., Amalia 3.0 x 10^{-6} cc./gm.). It is possible that Goamus was originally the centre of a meteoroid of mass 5×10^4 kg. and that Amalia was 80 cms. further out i.e. on the edge of a sphere of radius 80 cms. and mass 1.5×10^4 kg. This latter value happens to be the total mass of all the Bethany meteorites discovered. Though the remaining 3.5×10^4 kg. seems to be rather a large quantity to disappear on passing through the earth's atmosphere. Analysis of two points in Amalia, 7 cms. apart, by Paneth did give a difference of 0.25×10^{-6} cc/gm helium. Bauer calculated that there would be a possible difference of 0.90×10^{-6} cc./gm. if these two points had been radially disposed 80 cms.

from the centre of a 5 x 10^4 kg. meteoroid.

He concluded from this evidence that the time of solidification of the parent planet must have been less than 6 x 10^7 years ago, otherwise the amount of uranium and thorium present in the Bethany Goamus meteorite would have produced more than the observed helium content. Because of the shorter time in which the cosmic rays have to produce the helium, the production will have to be 70 times the estimate given previously. Bauer considers this possible if there is a much greater cosmic ray flux in free space than near the earth's surface, and especially if secondary cosmic rays produce an appreciable number of α-particles as well.

To test the truth of Bauer's theory, we have analysed one or two meteorites for radical distribution of helium. In one meteorite, we have analysed samples taken from seven different places of the meteorite. In others, we have confined ourselves to outer edges and centre portions. With the Helium Apparatus in its present state of efficiency, 100 mg. samples can be measured with an accuracy of one per cent.

2. METHOD.

The method of dissolution of the meteorite, and purification and actual measurement of the helium liberated, has already been described as a typical experiment employing the Helium Apparatus (see Chapter 2, part 2).

The samples themselves were taken from the meteorites either by means of a drill or a hacksaw. Experiments by Paneth (P14, P4) have proved that heating the meteorite metal to 1000°C for three hours released only a small percentage of the helium - consequently the heat generated during the drilling or sawing of the material would not affect the release of gas to any extent.

3. EXPERIMENTAL.

(a) OXYGEN PRODUCTION.

In order to save time in the preparation of pure oxygen by the hydrogen peroxide method, it was decided to use cylinder oxygen and liquify this in a tube leading from the main oxygen line and equipped with a stop-cock. When sufficient oxygen had been liquified, the stop-cock was closed and the remainder of the gas plus helium and most of the neon pumped away. At frequent intervals the stop-cock was openåd quickly and closed again. This produced sudden boiling of the liquid oxygen and consequent flushing out of dissolved neon in it. After repeating the process five,or six times the oxygen line was closed to the pumps and the liquid allowed to evaporate.

However, after several unsuccessful blank experiments when in each case a large amount of neon was detected, the method was abandoned and we reverted to the hydrogen peroxide method again. We can only conclude that neon is so soluble in liquid oxygem, that prolonged boiling and evacuation would be necessary to completely remove it. It was quicker and simpler to prepare pure oxygen from peroxide.

(b) DISSOLUTION OF THE METEORITE.

A most suitable concentration of acid was found by dissolving 200 mg. of meteorite filings in varying concentrations of acid, with and without potassium persulphate.

The ideal solvent (for the three meteorites we analysed at any rate) was estimated to be 5 cc. concentrated H_2SO_4 with 50 cc. water and saturated with persulphate. Because persulphate in solution slowly decomposes to the hydrogen sulphate and oxygen, freshly prepared solutions were necessary to avoid making the metal passive and hence insoluble. When a metal becomes passive, an invisible layer of oxide covers the whole surface preventing further dissolution, until the oxide layer is penetrated ,either mechanically or chemically. Such ions like persulphate and chloride are capable of doing this, and therefore assist in dissolving the metal. Using a saturated solution, 200 mg. metal can be dissolved completely within 20 minutes.

4. RESULTS.

(a) SPECIMEN CALCULATION.

Meteorite — SACRAMENTO MOUNTAINS (C - centre)

Weight of Meteorite = 0.1588 gm. - completely dissolved in 15 minutes.

Calibration for Helium.

P = 3.440 cms. at 22.6°C. $V = 8 \times 10.88 \times \left[1 - (22.6-20) \right] \times 10^{-8}$ cc.

$= \underline{2.964 \times 10^{-6}}$ cc.

Deflections.

(1) 23.74 cms. between 42 and 18 of scale

Scale corr. = +.05

True reading = 23.79 cms.

(2) 23.67 cms. between 42 and 18 of scale

Scale corr. = +.05

True reading = 23.72 cms.

(3) 23.47 cms. between 38 and 14 of scale.

Scale corr. = +.26

True reading = 23.72 cms.

(4) 23.44 cms. between 38 and 14 of scale

Scale corr. = +.26

True reading = 23.70,cms.

The first two calibrations were carried out before the measurement of the helium from the meteorite, and the second two afterwards.

Mean deflection = 23.73 cms.

Since 1% of the calibration helium is lost after 4 cupfuls have been removed from the calibration system, we must add ½% to the mean deflection to obtain the true deflection.

Therefore, true deflection is 23.72 + ½%

= 23.85 cms.

Therefore, He sensitivity $= \dfrac{2.964 \times 10^{-6} \text{ cc.}}{23.85}$

$= \underline{1.243 \times 10^{-7} \text{ cc./cm.}}$

<u>Helium from Meteorite.</u>

Operations 13-24 14.06 cms. between 45 and 31

Scale corr. -.34

True reading = 13.72 cms.

Operation 25 0.16 cms.

Operations 26-35 Negligible.

Previously we had discovered that the capillary tubing connecting the last bulb of the fractioating column to the Pirani space was not small compared with the volume of the Pirani space. In actual fact it is one per cent of total volume, and unless this amount is allowed to expand into the whole Pirani space after measurement of the helium fraction, it will appear in the neon fraction. That is the reason for measuring up to the 24th fraction first and then measuring the 25th on its own.

Total Helium Deflection = 13.88 cms.

Therefore, He/gm. meteorite $= \dfrac{13.88 \times 1.243 \times 10^{-6}}{.1588}$

$= 10.86 \times 10^{-6}$ cc./gm.

(b) TABLES OF RESULTS.

Meteorite - SACRAMENTO MOUNTAINS.

Sample	He x 10^{-6} cc./gm.
A (edge)	11.0
"	10.9
B (edge)	10.9
"	10.8
C (centre)	10.9
"	10.9
D (centre)	11.0
"	11.2
E (edge)	11.1
"	11.3
F (edge)	11.9
"	11.8
P (centre)	11.6
"	11.5

Meteorite - THUNDA.

Samples.	He x 10^{-6} cc./gm.
Edge	30.8
Centre	30.3

Meteorite - TOLUCA

Sample	He x 10^{-6} cc./gm.
Edge (inner slice)	20.5
Centre " "	19.9
Edge (outer slice)	19.4
Edge (outer slice, different part)	20.7

Other Meteorites.

	He x 10^{-6} cc./gm.
Bethany	0.14
Serrania de Varas (small meteorite)	14.00
Staunton	0.85
Treysa	25.1

(c) DISCUSSION.

Bauer's theory can be discussed clearly if his facts are divided under five separate headings, as follows:-

(i) ACTUAL AMOUNT OF HELIUM PRODUCED BY COSMIC RAYS.

Using the formula N = nJ/L, we obtain $\frac{1 \times 1.5}{150} \times 60 \times 60 \times 24$

$$= 1.18 \times 10^{-8} \text{ cc. Helium.}$$

Now Fowler (unpublished work), who has recently carried out observations on the production of "stars" on photographic plates by cosmic rays at high points in Switzerland and also on balloon flights, has postulated that in free space 6,000 stars/cc. emulsion/day will be obtained. The number of α-particles per disruption is on the average 1.5 and since the density of the emulsion is 4, then the number of α-particles per gram emulsion per day is 2250. The equivalent number which will be produced in iron of density 7.8 will therefore be 1150α s/gm. met./day. In 10^6 years this will give 1.56×10^{-8} cc. Helium, a value 25% higher than Bauer's.

Bauer's figure?

Why?

The equivalent amount of helium which would be produced by 1×10^{-8} gm. uranium plus 4×10^{-8} gm. thorium in the same time is 0.24×10^{-8} cc. Thus cosmic rays produce α-particles in iron 5 or 6 times more rapidly than the average quantity of uranium and thorium already present in meteorites.

More than this

The action is sufficient to account for all the helium in the richest meteorite known, in a time less than the assigned age of the Solar

System. Taking into consideration the share of the helium by the uranium and thorium, the age of meteorites will be much less than previously estimated.

(ii) SMALL METEORITES.

Because cosmic rays will not be absorbed to any great extent very small meteorites will contain the maximum helium content, providing one assumes that all meteorites were born from the parent planet at the same time.

(iii) LARGE METEORITES AND RADIAL DISTRIBUTION OF HELIUM.

On the same basis as the postulate in (ii), there should be very little helium near the centre of large meteorites and practically no radial distribution near the centre. For example, if we take the helium content of a small meteorite as 40 x 10^{-6} cc./gm., then in the centre of a meteorite of mass 10^4 kg., the helium content will be about 0.03 x 10 x 10^{-6} cc./gm. = 1.2 x 10^6 cc./gm. For 10 or even 20 cms. from the centre this amount will vary very little, until about 40 cms. the amount will have increased to about 0.1 x 40 x 10^{-6} cc./gm. = 4.0 x 10^{-6} cc./gm., and from there to the edge will increase rapidly to a value a little over 0.5 x 40 x 10^{-6} cc./gm.

(iv) METEORITES OF THE SAME NAME.

According to Bauer, it is no longer necessary to separate meteorites which have the same composition and found near each other. The particular meteorites he had in mind, of course, were the Bethany ones.

(v) AGE OF METEORITES AND THE PARENT PLANET.

Because of the small helium content of the Bethany meteorites and the established uranium and thorium contents the age of the Earth[11] cannot be more than 6 x 10^7 years.

Taking these points in order, we find we can add little to (i).

We have analysed a small meteorite Serrania de Varas, (original mass about 1.5 kg., diameter about 8 cm.); and discovered the helium content to be only 14×10^{-6} cc./gm. This helium content is only 1/3 of the maximum content so far discovered; so, unless the meteorite was originally the centre of a reasonably large one, we can say that the theory breaks down at this point. If the meteorite had been the centre of a large meteorite, from Bauer's graph this must have been at least 10^2 kg. Consequently more than 98 per cent by weight would have been lost in passing through the atmosphere.

In the case of (iii), if we consider a meteorite having a helium content of 11×10^{-6} cc./gm. at its centre, the radial variation must be several per cent over distances of 10 cms. The mass of the meteorite Sacramento Mountains is 25 kg. It is possible, if one considers Bauer's graph again, that nearly 9/10ths of the meteorite has been lost in the atmosphere making the pre-atmospheric mass equal to 250 kg. This corresponds to a sphere of radius about 20 cms.

To find out how much we should obtain 7 cms. from the centre of this sphere, we can substitute the appropriate figures into Bauer's equation:-

$$\frac{N(r)}{N_0} = \frac{1}{4r}\int_{R-r}^{R+r} e^{-d/D}\,dd + \frac{R^2-r^2}{4r}\int_{R-r}^{R+r}\frac{e^{-d/D}}{d^2}\,dd$$

This when evaluated, and providing d is not too big, is

$$\frac{1}{4r}D\left[\frac{-d/D\,(2-d/D)}{2!} + \frac{(d/D)^3(4-d/D)}{4!} + \frac{(d/D)^5(6-d/D)}{6!} + \frac{(d/D)^7(8-d/D}{8!} \;\ldots\ldots\right]_{R-r}^{R+r}$$

$$+\ \frac{R^2-r^2}{4r}\ \Big\{-\frac{1}{d}-\frac{1}{D}\,\ln d + \frac{1}{D}\Big[\frac{d/D(6-d/D)}{1\mathrm{x}2\mathrm{x}3!} + \frac{(d/D)^3(20-3d/D)}{3\mathrm{x}4\mathrm{x}5!} + \frac{(d/D)^5(42-5d/D)}{5\mathrm{x}6\mathrm{x}7!}$$

$$+ \frac{(d/D)^7(72-7d/D)}{7\times 8\times 9!} \;\ldots\ldots \Bigg]\Bigg\}_{R-r}^{R+r}$$

when R = 20, r = 7

$$\text{Above} = \frac{19.2}{28}(0.412 + 0.308 + 0.185 + 0.010) - \frac{19.2}{28}(0.449 + 0.044 + 0.006)$$

$$+ \frac{351}{28}\left[-0.037 - 0.172 + \frac{1}{19.2}(0.542 + 0.031 + 0.001)\right] - \frac{351}{28}\left[-0.077 - 0.137\right.$$

$$\left. + \frac{1}{19.2}(0.303 + 0.004)\right]$$

$$= 0.288 + 0.25$$

$$= \underline{\underline{0.54}}$$

Consequently, should Bauer's theory be correct, we should expect to find 0.54 x 40 x 10^{-6} cc./gm. 7 cms. from the centre of the sphere.

We certainly did not find this experimentally. In fact, the figures for Sacramento Mountains show very little deviation between the points, A, B, C, D, and E, three of which were edge samples and the other two centre ones. P and F agree with one another, but being from another part of the meteorite the difference between the mean value and the mean value of A, B, C, D, and E, which is 7% can be accounted for by inhomogeneity of the distribution of uranium and thorium. This, naturally, cannot be checked at present.

It can be recorded here, that we were surprised at finding the results in such good agreement, indicating good homogeneity at least in large areas of the meteorite. It is possible that the other piece of Bethany on which Paneth carried out his experiments was inhomogeneous; but only one determination was carried out, and it may have been purely coincidence that the value ontained for the centre portion was somewhat less than the edge sample. No such far reaching conclusions as those of Bauer should be based on this one figure.

The meteorite Thunda, whose mass was about 6 kg., may have had a pre-atmospheric mass of 10-20 kg., in which case the present outer edge should contain about 0.85 x 40 x 10^{-6} = 34. x 10^{-6} cc./gm. compared with 30 x 10^{-6} cc./gm. in the centre. Our value differed by less than 2% from the centre value.

The same may be said about the metorite Toluca, which corresponds to a pre-atmospheric mass of probably 70-80 kg. according to Bauer's graph. Professor Paneth possesses an outer slice from an unknown meteorite which for various strong reasons is supposed to be part of the block of the meteorite Toluca of which an inner slice is in the Science Museum (British Museum, Natural History). We have measured the helium contents of both and they are identical. If our surmise is correct, the original mass (not the pre-atmospheric) would have been between 1800 and 1000 kg. The meteorite of mass 80 kg. having 20 x 10^{-6} cc./gm. of helium at the centre, should have at least 30 x 10^{-6} cc./gm. at 14 cms. from the centre. We found practically no difference between the outer edge and the centre.

Bauer's hypothesis that the Bethany meteorites all belong to one fall and that the different helium contents are due to radial distribution of helium, need not be accepted on the fact that the composition of Bethany (Goamus) and Bethany (Krantz) are identical. All meteorites have practically the same amounts of uranium and thorium, and because experimental evidence gave exactly the same figures in these two cases, we cannot state definitely that they belong to the same meteorite. Paneth in his paper of 1942, states that 10% accuracy could be obtained with 30 gr. samples in the case of the radioactive measurements. Samples varying in weight between 15 and 20 grms. were actually used, consequently the accuracy may have only been 15 - 20%. It is quite possible that Bethany Amelia (Krantz) is a different fall from the other Bethany blocks. Dr. Chackett has determined 6 Chilean meteorites which contain helium varying between 0.56 and 2.00 x 10^{-6} cc./gm. Yet from other evidence one would guess that they all came from the same fall.

Finally, on point (v), Bauer accounts for the small helium content in Bethany Goamus, reputed to be the centre portion of a 5 x 10^{4} kg. meteorite, by stating that the maximum age since solidification and presumably since the breakup of the parent planet, was 6 x 10^{7} years ago. But there are other meteorites containing far less helium, namely the Cape York meteorite with less than .001 x 10^{-6} cc./gm. and a Swedish one, Monionalusta, determined by Dr. Chackett, with less than .002 x 10^{-6} cc./gm. Presumably these meteorites contain uranium and thorium, because they are undoubtedly meteoritic. Even if they contained only one tenth of the average amount of radioactive material, the greatest possible age would only be 3 or 4 x 10^{6} years. So unless Bauer is prepared to increase the value for Cosmic ray flux to proportions as much as 1,000 or even a few thousand times his present factor, his statement regarding the maximum age of the parent planet must be reviewed. Increasing this to such proportions, however, makes his quantitative work so far valueless.

We must face the possibility that the cosmic ray effect as we find it in the earth's atmosphere has not the same effect in outer space. It may produce helium in meteorites, but be so powerful that absorption by twenty or more cms. of iron is negligible.

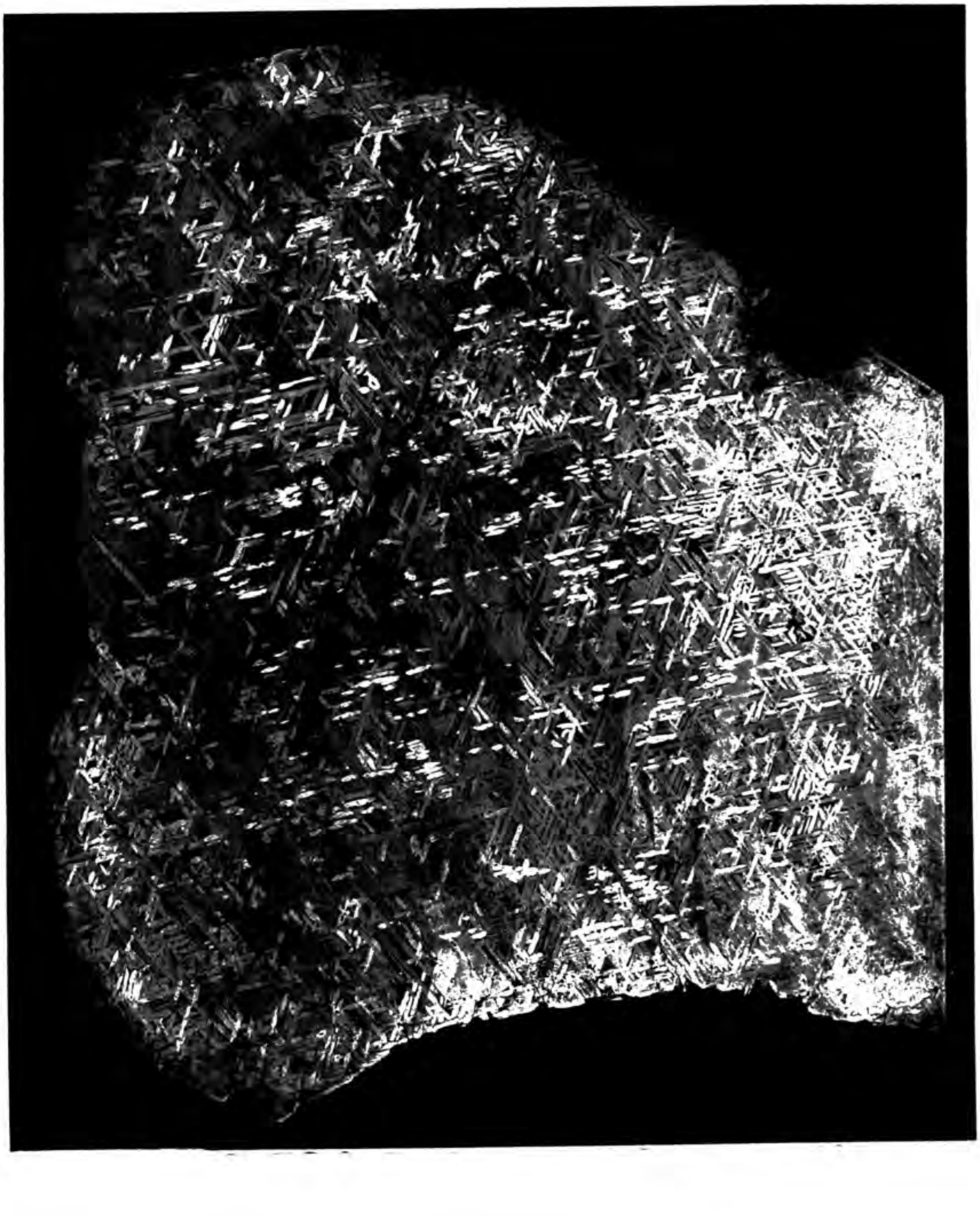
On the other hand, we may say that the breakup of the parent planet of the meteorites was a very recent event. This will account for the very low helium contents, unless they were remolten at some stage, because no small body like a meteoroid can remain in a molten state for long. If we are to accept the fact that the age of the solar system is no more than 3,500 million years, then a process as unknown at present as that operating in beryls, must account for the "excess helium".

Though we have proved that helium does not vary radially in three different meteorites, to really test the Bauer effect, a He^3/He^4 ratio of meteorite helium should be carried out. Absence of He^3 would almost certainly exclude cosmic ray action.

5. CONCLUSION.

We have shown experimentally by dissolving 100 mg. samples of meteorite taken from the centre and outer edge of three meteorites, that the "Bauer effect" does not exist. Our results agree to within 1 or 2%, and within these limits there is no difference in the mean helium content of outer and centre samples.

Measurement of the He^3/He^4 ratio in meteoritic helium should definitely prove the existence or non-existence of the Bauer effect.



TOLÚCA METEORITE.

SACRAMENTO MOUNTAINS METEORITE (Showing drill holes).

CHAPTER 6.

THE HELIUM CONTENTS OF BERYLS AND MAGNETITES.

1. INTRODUCTION.

In the Historical introduction to this thesis, it was explained that Beryls are the only minerals of terrestrial origin which have extremely high helium contents compared with the amount of radioactive material present. Various investigators have attempted to explain this phenomenon, including Lord Rayleigh and Paneth.

It was suggested by Rayleigh, after he had proved that the helium excess could not be ascribed to a radioactive α-emitting element which had disappeared during geological time, by showing that large helium contents were limited to specimens of great geological age, that the helium must come from another element besides uranium or thorium.

This problem has been tackled by E.R. Mercer of this department, who carried out analyses on many beryls and concluded that the helium contents are not proportional in any way to the amount of any of the other elements present. It was in conjunction with this work that the helium contents of two beryls were confirmed using the Helium Apparatus.

Magnetites are other minerals which have a high helium content, which may however be explained by the very high retentivity of the mineral for this age. The helium estimation of one magnetite has been carried out to determine whether or not it was of Pre-Cambrian origin. The radium and thorium analyses were carried out by Mr. Mercer.

2. METHOD.

Liberation of helium from beryls by heating alone in the absence of air were attempted first, and later with caustic potash as a flux.

A small crystal of the beryl was chipped off and weighed, put in a platinum furnace and a gram or two of potash previously melted to get rid of occluded air, added. The furnace was immediately attached to the Helium Apparatus and evacuated. (Platinum is not attacked by caustic if heated with it in absence of oxygen.) The furnace was raised to a temperature of 700°C and maintained there for about 3/4 hour.

Before cooling, pure oxygen was introduced quickly to flush out the Helium and other gases produced during fusion, into the circulating part of the Helium Apparatus. Purification and measurement were carried out in the normal way.

In the case of the magnetite, it was found better to use finaly ground powder together with fusion mixture and prolong the heating for 3 hours. Experiments conducted by Paneth in 1936 (H2), showed that very little helium is lost through powdering rocks and minerals if the helium determination is carried out shortly afterwards.

3. EXPERIMENTAL.

Experiments were carried out with two beryls, one from Pisek (Norway) and reputed to contain 4.75 cu.mm. Helium/gram, and the other from Leydsdorp (Transvaal) reputed to contain 29.2 cu.mm. Helium/gram.

Approximately 7 mg. of the beryl were accurately weighed out, and heated alone for half an hour at 700° C. The amount of helium liberated was only 2 per cent of Rayleigh's figure. Further heating for another ½ hour released a negligible amount.

In the next experiment anout 1 mg. was employed and heated with about 2 grams of potash for 3/4 hour, and the helium liberated shown to be half that of Rayleigh's. Since the object of the experiment was only to check the ~~the~~ order of the result, no more experiments were carried out with the beryl.

The same method was applied to the second beryl and in the case of the magnetite sufficient detail has been given above.

4. RESULTS.

(1) Beryl - PISEK (Norway).

Weight of Beryl = 0.0013 gm.

Helium calibration - 4.14×10^{-8} cc./cm. deflection.

Helium content = 67.5 cms.

Therefore, Helium per gm. beryl $= \dfrac{67.5 \times 4.14 \times 10^{-8}}{0.0013}$

$= \underline{\underline{2.38 \text{ cu. mm/gm.}}}$

(cf. Rayleigh - 4.47 cu. mm./gm.)

(2) Beryl - LEYDSDORP (Transvaal).

Weight of Beryl = 0.00232 gm.

Helium calibration = 2.97×10^{-7} cc./cm.

Helium content = 213 cms.

Helium per gram. beryl $= \dfrac{213 \times 2.97 \times 10^{-7}}{0.00232}$

$= \underline{\underline{27.3 \text{ cu. mm./gm.}}}$

(cf. Rayleigh - 29.2 cu. mm/gm.)

(3) Magnetite - ANGOLA.

Weight of magnetite = 0.1201 gm.

Helium calibration

P = 7.7077 cms. at 20.2oC. $V = 8 \times 7.077 \times 10^{-8}$ cc =

$\underline{\underline{5.66 \times 10^{-7} \text{ cc}}}$

Deflections

(1) -3.78 cms. between 41 and 37 of scale.

Scale correction = -.09 cms,

True reading = 3.69 cms.

(2) -3.71 cms. between 41 and 38 of scale

Scale correction = -.07

True reading = 3.64 cms.

Mean = 3.67 cms. + ¼% = 3.68 cms.

$$\text{Therefore Helium sensitivity} = \frac{5.66 \times 10^{-7}}{3.68}$$

$$= \underline{\underline{1.54 \times 10^{-7} \text{ cc./cm.}}}$$

Helium.

Operation 13 - 0.68 cms. between 41 and 40

Scale correction = -.02 0.66 cms.

Operations 14-16 - 9.81 cms. between 40 and 31

Scale correction = -.10 9.71 cms.

Operations 17-30 - 21.19 cms. between 41 and 20

Scale correction = +-07 22.26 cms.

Operations 31-40 - 0.69 cms. between 42 and 41

Scale correction = -.05 0.64 cms.

Now 1.5 per cent of the helium comes over after the 30th Operation.

$$\text{Therefore total He} = \frac{32.63}{.985} = 33.13 \text{ cms.}$$

Thus Neon due to air leak = 0.64 - 0.50 = 0.14 cms.

$\equiv$ 0.06 cms. He

This is negligible.

Therefore Helium from the Magnetite = 32.63 cms.

$$\text{He gm. of magnetite} = \frac{32.63 \times 1.54 \times 10^{-7}}{0.1201}$$

$$= \underline{\underline{4.10 \times 10^{-5} \text{ cc./gm.}}}$$

The uranium and thorium contents were 8.9×10^{-7} gm./gm. and 1.1×10^{-5} gm./gm. respectively, corresponding to an age of about 9.4×10^{7} years.

CONCLUSION.

The large helium content of two Beryls originally measured by Lord Rayleigh were confirmed by heating a minute crystal of beryl with caustic potash in a platinum furnace for approximately 3/4 hour at 700°C. Mere heating of the beryl alone was only capable of releasing about 2% of the occluded helium.

A magnetite of unknown age, but thought to be of Pre-Cambrian origin, was heated with fusion mixture for 3 hours to release all the helium. From the helium content and the uranium and thorium contents determined by Mr. Mercer, it was estimated that the magnetite was younger than of Pre-Cambrian origin.

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