

# XXIII. Experiments with the radium emanation. (1) The volume of the emanation

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XXIII. *Experiments with the Radium Emanation.* (1) *The Volume of the Emanation.* By E. RUTHERFORD, F.R.S., Professor of Physics, University of Manchester\*.

THE amount of radium emanation to be obtained from one gram of radium in equilibrium is a definite quantity, and is equal to  $q/\lambda$  where  $q$  is the rate of production of emanation per second and  $\lambda$  is the radioactive constant of the emanation. Taking the half period of the emanation as 3.75 days, the value of  $\lambda$  is  $1/468000$ . I have on different occasions† calculated the volume of the emanation (at normal pressure and temperature) to be expected from one gram of radium from the radioactive data at our disposal. As the simplest and most probable assumption, it is supposed that one atom of radium in breaking up emits one  $\alpha$  particle and then becomes an atom of the emanation. On the assumption that each  $\alpha$  particle carries the ordinary ionic charge  $e$  of  $3.4 \times 10^{-10}$  electrostatic unit, it was calculated that the volume of the emanation from one gram of radium should be 0.8 cubic millimetre. Later work‡ indicated the probability that the  $\alpha$  particle carried the charge  $2e$ . This reduces the calculated volume of the emanation to one-half of the above value. Recently, in conjunction with Dr. Geiger, the number of  $\alpha$  particles expelled per second from one gram of radium has been accurately determined, and also the charge carried by each  $\alpha$  particle. From these data, we have calculated that the volume of the emanation is 0.57 cubic mm.—a value about intermediate between the other two values§.

The first experiments to measure directly the volume of the emanation were made by Ramsay and Soddy||. The emanation after suitable treatment was condensed in a glass tube surrounded by liquid air. The residual gases were pumped off, and the emanation after volatilization was forced by raising the mercury into a capillary tube where its volume was measured. From the volume of the collected gas observed after two days, they concluded that the volume of the emanation was about 1.2 cubic mm. Later a number of systematic observations of the volume of the emanation by a similar method have been made by Ramsay and Cameron¶.

\* Communicated by the Author, having been read before the Academy of Sciences of Vienna, July 2, 1908.

† 'Radioactivity,' 2nd edition, p. 288.

‡ Rutherford, Phil. Mag. Oct. 1906.

§ An account of this work was given to the Royal Society, June 18, 1908.

|| Proc. Roy. Soc. lxxiii. p. 346 (1904).

¶ Journ. Chem. Soc. p. 1266 (1907).

They conclude that the volume of the emanation is about 7.07 cubic mms., and suggest that the smaller value initially obtained by Ramsay and Soddy was due to the greater part of the emanation being pumped off during the experiment. The volume of the emanation (7.07 cubic mms.) obtained in their experiments is of quite a different order from the calculated volume (0.57 cubic mm.). It is of importance to determine the cause of this wide discrepancy between theory and experiment. If the experimental value proves correct, it would indicate that much of the radioactive data and of the theory on which the calculations are based is seriously in error. Apart from the interest attaching to the comparison of theory with experiment, the separation of the radium emanation in a pure state is now of the highest practical importance. Not only is pure emanation required in order to study carefully the physical and chemical properties of this remarkable gas, but it is also required in the experiments similar to those initiated by Ramsay and Cameron \*, where the radium emanation is added to different solutions and the resulting products determined.

By the generosity of the Academy of Sciences of Vienna, I was recently loaned a preparation of radium containing about 250 milligrams of radium. Experiments were immediately begun in order to purify the emanation produced by it, and to determine its volume. In all, a large number of experiments have been made, but for brevity I shall here only indicate the general results obtained in these investigations.

### *Separation of the Emanation.*

There are two general methods of obtaining the emanation from preparations of radium, viz., by heat or by solution. Both of these methods have been used. In the earlier experiments, the radium preparation was placed in a thin quartz tube which was enclosed in a larger quartz tube. The latter was heated to the desired temperature by means of an electric furnace. The emanation is practically all released at the temperature of fusion (about 830° C.) † of barium-radium chloride. After the preliminary heating, a very small quantity of intensely radioactive gas was released, the volume of which was so small that it was found necessary to add a small quantity of hydrogen or oxygen in order to pump off the emanation completely. In later experiments, the radium preparation was in solution in a quartz tube. The emanation

\* Journ. Chem. Soc. p. 1593 (1907).

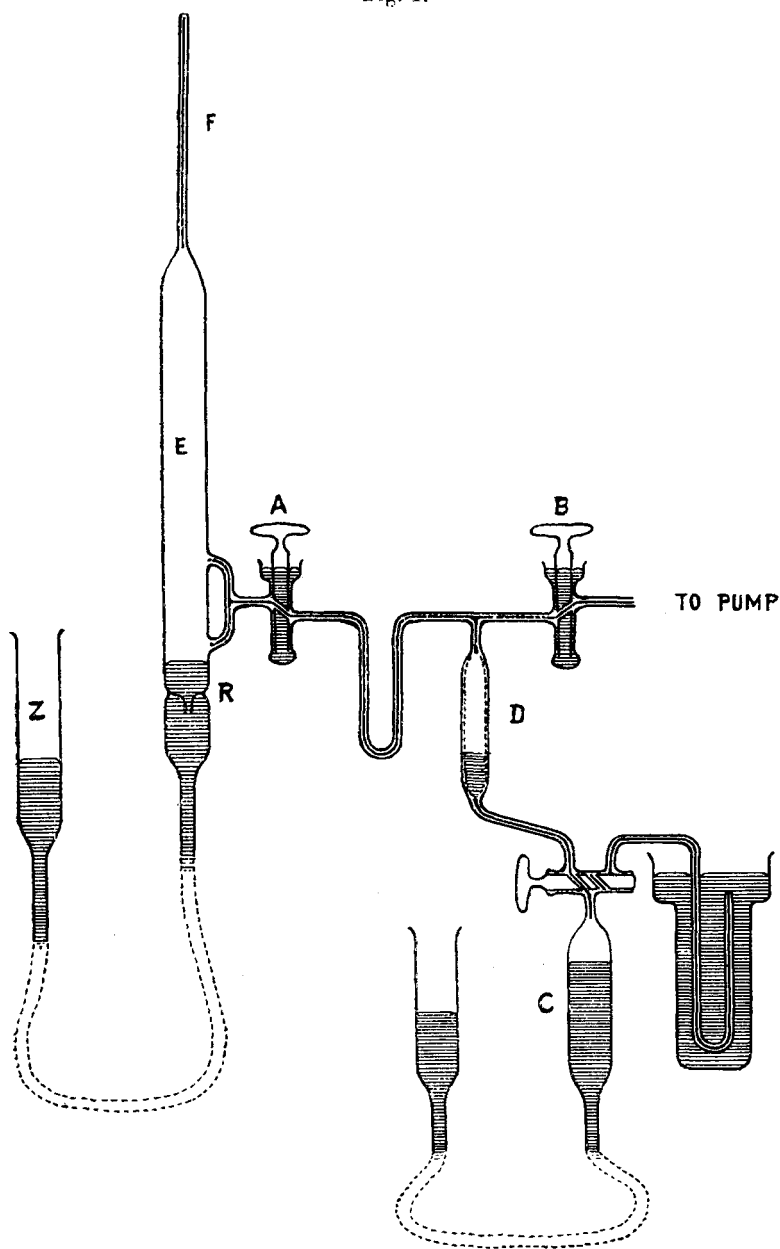
† See paper by L. Kolowrat, *Le Radium*, Sept. 1907.

was pumped off together with a large quantity of hydrogen and oxygen formed in solution. After the method employed by Ramsay and Cameron, this was sparked down and a small quantity of oxygen added in order to reduce the excess of hydrogen. The emanation, mixed with about 1 cc. of hydrogen, was then collected over mercury in a small burette in which was placed a piece of caustic potash in order to absorb any carbon dioxide present. The apparatus for purification of the emanation and measurement of its volume is shown in fig. 1. The measuring apparatus consisted essentially of a Macleod gauge. A capillary tube, 15 cms. long and 0.58 mm. diameter, was attached to a long glass tube of volume about 25 cubic cms. By raising the reservoir with the stopcock A closed, the gas in the tube E was forced into the capillary tube F and its volume measured. A mercury trap R was used to avoid the entrance of any gas which crept along the surface of the glass. The general method of purification of the emanation is best seen from a description of an experiment\*.

The whole apparatus was first exhausted to a low vacuum by means of a mercury pump. The emanation, conveyed with about 1 cc. of gas, was transferred over mercury into the reservoir C. The stopcocks A and B were closed, and the emanation was forced by raising the mercury reservoir through the stopcock H along the tube D, coated with caustic potash, into the U-tube T. The U-tube, of volume about 1.5 c.cms., was surrounded by liquid air in order to condense the emanation. The whole emanation was condensed by successively raising and lowering the mercury in the reservoir. The stopcock B was then opened into the pump and the uncondensed gases completely pumped off. The mercury was then lowered in the tube D to the position of the dotted line in the figure. The liquid air was then removed. The emanation after volatilization was left some hours in contact with the caustic potash in the tube D to remove the last trace of carbon dioxide. The U-tube was then surrounded by a vessel filled with pentane, which was cooled down by liquid air to a temperature between the temperature of condensation of the emanation ( $-150^{\circ}$  C.) and the temperature of liquid air ( $-186^{\circ}$  C.). The whole apparatus was then completely exhausted again by the mercury pump, a portion of the emanation being volatilized during the process and removed by the pump. Finally, when a very low vacuum was

\* In this work, I have found the methods developed by Ramsay and others for manipulating small quantities of gases of great assistance. See Travers, "Study of Gases."

Fig. 1.



obtained, the liquid air was removed, the stopcock B closed, and the emanation after volatilization was allowed to expand into the tube E. Since the volume of the U-tube was small compared with the tube E, the greater part of the emanation after volatilization expands into the tube E. The experiments were made in a darkened room, so that the moment of almost complete volatilization of the emanation could be observed by the sudden phosphorescence of the tube E due to the entrance of the emanation. The stopcock A was then closed and the emanation forced into the capillary, where its volume was measured at regular intervals.

*Activity measurements.*

In this type of experiment, it is of importance to determine accurately the amount of emanation in the capillary where the volume is measured. This was done by comparison of the  $\gamma$  ray activity due to the emanation in the capillary with that due to a standard sample of radium bromide which gave a heating effect of 110 gram-calories per gram per hour. When the emanation had been forced into the capillary, the residual emanation in the U-tube and connexions was completely pumped out and all sources of  $\gamma$  rays removed to a distance. A small closed lead electroscope was placed at a distance of 76 cms. from the emanation in the capillary, and the rate of discharge observed about three hours after the introduction of the emanation. The  $\gamma$  ray activity compared with a standard is then a measure of the amount of emanation expressed in terms of the equilibrium quantity present in one milligram of pure radium. Measurements were made daily of the  $\gamma$  ray activity of the emanation. Experiment showed that the highly concentrated emanation compressed into a small volume had the usual rate of decay, viz. half period in 3.75 days. Measurements of this character are essential if any accuracy is required. It is not sufficient to assume that all the emanation formed in a certain interval of days is pumped off from the radium solution. Moreover a small part of the emanation is left behind in every operation of transferring the emanation from one vessel to another. It may be mentioned that in most of the experiments the amount of emanation whose volume and activity were measured was equivalent to the equilibrium quantity from 60 to 140 milligrams of radium. Usually the amount of emanation pumped off during the experiment corresponded to 20 or 30 milligrams of radium.

*Discussion of Experiments.*

Preliminary experiments showed that the volume of the emanation was certainly much lower than that found by Ramsay and Cameron; the purity of the emanation was examined spectroscopically in the capillary itself without the use of electrodes. Some tinfoil was wound round the upper and lower part of the capillary and a discharge produced in the capillary by means of a small induction-coil. The spectrum was examined by a Hilger spectroscope, by means of which the wave-length of the lines could be read off directly. In the preliminary experiments, the spectrum observed was the ordinary band spectrum ascribed to carbon dioxide with some of the mercury lines and occasionally a few other very faint lines. Precautions were then taken to get rid of the carbon dioxide. Phosphorus pentoxide instead of tap grease was used to lubricate the stopcocks. The emanation was always left in the presence of solid caustic potash some time before its introduction into the U-tube. In addition the emanation after the uncondensed gases were pumped off was left in contact with the tube D which was coated with a layer of caustic potash. Notwithstanding all these precautions it was found at first impossible to remove the last traces of carbon dioxide. Attempts were made to remove the greater part of the residual  $\text{CO}_2$  by fractional distillation, using the pentane bath for temperature adjustment, but with only partial success. There appears to be some evidence that the emanation prefers to condense with the  $\text{CO}_2$  which is present, and is released with it when the temperature rises. Finally, after a large number of experiments, it was found essential to allow the emanation after purification from other gases to remain five or six hours, preferably 24 hours, in the presence of the caustic potash tube D. When this was done, it was found that the volume of the gas obtained in the capillary was much reduced and the carbon-dioxide spectrum became much fainter. The reason why such a long time of exposure to caustic potash is required is not at all clear. It may be due to the very slow absorption of the last traces of carbon dioxide by caustic potash. It is possible, however, that the spectrum ascribed to  $\text{CO}_2$  is in reality due to carbon monoxide in the presence of oxygen. There is considerable difference of opinion among spectroscopists on this point. If the disturbing gas is CO it must first be converted into  $\text{CO}_2$  in the presence of oxygen by the action of the emanation before absorption by the caustic potash. This would account for the long time required for complete absorption. As far as my experience

has gone, the essential conditions for the purification of the emanation depend upon the pumping off the residual gases at a temperature below the temperature of volatilization of the emanation and considerably above the temperature of liquid air; and the long exposure of the emanation to caustic potash. By the former method practically all the known inactive gases would be pumped off. I think the high value of the volume of the emanation obtained by Ramsay and Cameron must be ascribed to the presence of other gases besides the emanation, which are condensed at the temperature of liquid air.

### *Changes in Volume.*

Ramsay and Cameron (*loc. cit.*) have given a number of examples of the changes in volume observed in their experiments to measure the volume of the emanation. The volume of the gas in the capillary usually diminished with time rapidly during the first two hours to about half value and then more slowly. I have observed very similar effects in my experiments, using impure emanation. In some cases the volume diminished in the course of several hours to less than half value, but after this preliminary decrease little change was observed in the volume over the further interval of a week. In other experiments, the volume increased instead of diminishing in the course of a few hours, sometimes increasing to twice the initial volume, followed later by a slow decrease with time. The expansion or contraction of the volume has in many cases no direct connexion with the volume changes of the emanation itself, for the true volume of the emanation present was in some experiments certainly not more than 20 per cent. of the total\*. It is difficult to explain these expansions and contractions except on the supposition that the gases mixed with the emanation either combine or dissociate under the influence of the powerful radiation from the emanation. Until experiments are made with some known gas or gases added to pure emanation, we can only speculate upon the nature of the gases present and the combinations or dissociations which are effected. There is another possibility which may prove to be an important factor in the volume changes, especially with nearly pure emanation. It is believed that the positive and negative ions produced in a gas at

\* Ramsay and Cameron explained the decrease of volume observed in their experiments on the assumption that the emanation changed from a monatomic to a diatomic gas. Since the volume in these experiments certainly contained less than 20 per cent. of emanation, the explanation is inadmissible.



ordinary pressure have a cluster of molecules attached which move with them. Since the emanation itself and the gases associated with it are intensely ionized, it is possible that the effective volume may be decreased due to the production of a large number of these aggregates. On this view, the decrease of volume observed during the first two hours may be partly due to the increase of the number of these aggregates consequent upon the increase of the radiation from radium C.

### *Experimental Results.*

We shall now give some typical examples out of a number illustrating the initial changes in volume. The capillary tube used in all the experiments was of Jena borosilicate glass of very uniform bore, 0.58 mm. in diameter. The capillary correction was equal to 14 mm. of mercury. The tube was slowly coloured brown by the emanation. By heating the tube to the temperature of thermo-luminescence, the glass again became quite clear. The capillary was heated at the beginning of each experiment to drive off residual gases. The gases in the capillary in all cases obeyed Boyle's law over the range examined within the limit of experimental error.

*Experiment I.*—This illustrates the increase of volume observed for very impure radium emanation. The amount of emanation in the capillary, determined by direct measurement, corresponded to 67 mgrs. of pure radium.

Time after introduction of the emanation into capillary.	Volume of gas in capillary at standard pressure and room temperature.
2 minutes	0.154 c.mm.
6 "	.169 "
17 "	.201 "
28 "	.235 "
41 "	.260 "
50 "	.270 "
64 "	.280 "
71 "	.291 "
81 "	.297 "
3.9 hours	.346 "
21 "	.355 "

At the end of 24 hours the spectrum of the gas was examined in the capillary. The carbon dioxide spectrum

was prominent. In addition to the mercury lines, a few others were observed which were not identified with certainty. The initial volume, 0.154 c.mm., corresponded to 67 mgs. radium, consequently the initial volume corresponding to one gram of radium was 2.3 c.mm. The final volume after 21 hours corresponds to 5.2 c.mm. per gram. As the spectrum indicated, the emanation in this case was very impure, containing probably a large proportion of CO or CO<sub>2</sub>.

*Experiment II.*—We shall now give an example of the contraction of volume. In this case the emanation was far purer than in experiment I. The emanation was left four hours in the presence of caustic potash before introduction into the capillary. The amount of emanation in the capillary corresponded to 130 mgs. radium.

Time after introduction of the emanation into capillary.	Volume of gas in capillary at normal pressure and room temperature.
2 minutes	0.171 c.mm.
5 "	.169 "
10 "	.165 "
18 "	.158 "
26 "	.150 "
37 "	.135 "
56 "	.126 "
70 "	.120 "
91 "	.106 "
5.9 hours	.097 "
17 "	.069 "
44 "	.075 "
92 "	.079 "
161 "	.080 "
185 "	.119 "
209 "	.125 "
257 "	.125 "

The initial volume for the emanation from one gram of radium corresponded to 1.32 c.mm. Correcting for the decay of the emanation, the volume at the minimum after an interval of 17 hours was equal to 0.59 c.mm. per gram of radium. It will be observed that the volume sank to about 0.4 of its initial value after 17 hours. After passing through a minimum, the volume increased again, though not very regularly. At the conclusion of the experiment, *i.e.* after

the emanation had remained nearly 11 days in the capillary, the spectrum of the gas was examined in the capillary as described above. *A brilliant spectrum was obtained showing all the lines of helium.* The spectrum of  $\text{CO}_2$  was also observed, although weak in intensity compared with that of helium. In addition to the mercury lines, a few unidentified bright lines were noted. This result is a confirmation of the well-known experiment of Ramsay and Soddy, who found that the spectrum of helium appeared after some time in a tube containing radium emanation. The cause of the increase of volume after the minimum is now clear. Assuming that the  $\alpha$  particles are atoms of helium, the helium would at first be fired into the glass. After a time part of it gradually escaped and added its volume to the emanation and other gases present. It is difficult to be certain how much of the helium was retained in the glass of the capillary. If we take the initial volume of the emanation to be about that observed at the minimum volume, viz. .059 c.mm., the volume of helium to be expected is about three times this amount. This is on the assumption that each  $\alpha$  particle expelled is a helium atom. The final volume observed after 11 days was .125 c.mm., and was probably mainly due to the helium.

*Experiment III.*—In this case the emanation was very carefully purified, after standing for 18 hours over caustic potash. The amount of emanation present corresponded to 130 mgs. radium. The initial volume of the emanation was .097 c.mm. This corresponds to a volume of 0.80 c.mm. per gram of radium. No certain change in volume was observed over an interval of 15 minutes. The emanation was then recondensed in the U-tube, which was pumped out again using a pentane bath. On introducing the emanation into the capillary again, very nearly the same initial volume as before was observed. In order to test the purity of the emanation, the spectrum of the gas in the capillary was examined. A new spectrum of bright lines, certainly due to the emanation itself, was observed. Some of the bands of the carbon dioxide spectrum were observable. Observations were at once begun to determine the wave-lengths of the new lines with accuracy. Before this was completed, most of the lines due to the emanation suddenly ran out, and the carbon dioxide spectrum became more prominent. The volume of the gas in the capillary was also found to have considerably decreased. It was then observed by the phosphorescence that the emanation was adhering to the walls of the capillary, and only a part of the emanation was free in

the gaseous state. The emanation remained fast to the walls for two days, and was only removed finally by a vigorous heating of the tube. It appears that the emanation must have been driven into the walls of the tube or occluded in it under some condition due to the passage of the discharge.

*Experiment IV.*—In this case the emanation, after the initial purification, was left five hours over caustic potash. After introduction the initial volume was  $\cdot 126$  c.mm. The volume remained nearly stationary for 20 minutes and then slowly diminished, reaching a value of  $\cdot 076$  c.mm. after 17 hours. The amount of radium emanation initially present was 130 mgs. radium. The initial volume of emanation thus corresponded to  $0\cdot 97$  c.mm. per gram of radium, and the lowest volume, allowing for the decay of the emanation in the interim, corresponded to  $0\cdot 66$  c.mm. per gram.

*Experiment V.*—The emanation used in experiment IV. was again condensed in the U-tube and then left for 24 hours in the presence of caustic potash. The emanation after further treatment was admitted into the capillary. The initial volume was  $\cdot 083$  c.mm. As in the case of experiment IV., the volume remained nearly stationary for 20 minutes and then slowly decreased. The volume after 4 hours was  $\cdot 046$  c.mm. The amount of radium emanation in the tube was equal to 79 mgs. radium. Consequently the initial volume of the emanation per gram was  $1\cdot 05$  c.mm., and the volume after 4 hours  $0\cdot 58$  c.mm. The spectrum of the gases in the capillary was then examined. As before the carbon dioxide spectrum was seen together with a number of new lines due to the emanation, the wave-lengths of which were measured. No trace of the hydrogen lines was observed in this or in the other experiments. After the discharge had passed at intervals for two hours, most of the lines due to the emanation disappeared. The greater part of the emanation was then found to be sticking to the surface of the capillary, as in the previous experiment. The prominence of the carbon dioxide spectrum cannot I think be ascribed to the presence of a considerable amount of this gas mixed with the emanation before the discharge passed, but rather to the production of this gas by the discharge, due probably to the presence of a trace of some organic matter at the surface of the mercury. The correctness of this view was confirmed by the observation that the spectrum of carbon dioxide was unaltered in brightness, after practically all the residual

gases and emanation had been removed by the pump\*. I hope in a later paper to give a more detailed account of these and other experiments to determine the spectrum of the radium emanation. In these investigations the spectrum has been obtained incidentally in the course of testing the purity of the emanation in the capillary.

*Summary of Results.*

For convenience, the results of experiments II. to V. on the volume of the emanation are collected below :—

Experiment.	Initial volume of emanation per gram of radium.	Final volume of emanation per gram of radium.
II. ....	1.32 c.mm.	0.59 c.mm.
III. ....	0.80 „	
IV. ....	0.97 „	0.66 „
V. ....	1.05 „	0.58 „

The volumes here given are at normal pressure and room-temperature (about 16° C.). If corrected to standard temperature, the volumes will be about 5 per cent. smaller. A small undetermined correction should also be applied for the heating effect of the emanation. We have already seen that the calculated volume at normal pressure and temperature is 0.57 c.mm.

From the above table it is seen, that the smallest initial volume of the emanation observed is 0.80 c.mm. per gram of radium, and the smallest volume after contraction 0.58 c.mm. The volume before contraction, observed by Ramsay and Cameron, was 7.07 c.mm. per gram. It was observed that the emanation was not appreciably absorbed in the capillary during the first few hours, provided a discharge was not passed, and was all released on lowering the mercury. For these reasons, it seems probable that the volume after contraction is to be taken as the true volume of the emanation rather than the volume in the beginning. On this view, there is as good an agreement as could be expected from the nature of the experiments between the final volumes,

\* Later observations have confirmed the correctness of this explanation. The emanation purified after the manner described was introduced in a spectrum-tube with platinum electrodes. No trace of the band spectrum of carbon dioxide has been observed in the spectrum produced by the discharge. (See accompanying paper "On the Spectrum of the Radium Emanation.")

viz. 0.59, 0.66, and 0.58 c.mm., and the calculated volume, viz. 0.57 c.mm.

We have already seen that it is difficult to offer a satisfactory explanation of the initial contraction. Before this can be done, a large number of further experiments will be required. The work outlined in this paper is merely preliminary, and it is hoped in a later paper to give the results of a more complete examination of the volume of the emanation and of the changes it undergoes.

*Remarks on the Condensation of the Emanation.*

When the emanation was obtained in a nearly pure state, it condensed exceedingly rapidly at any point cooled below the temperature of condensation ( $-150^{\circ}\text{C}.$ ). If the emanation were contained in the U-tube (fig. 1), the slow approach of the liquid air to the bottom of the tube caused the condensation in some cases to take place over an extremely small area, probably at a point where the tube was thinnest. A brilliant phosphorescent speck was then observed, and it almost appeared as if one could see the liquid emanation in the form of a flat globule condensed over an area of less than half a square millimetre. This effect was often observed and is very striking. After a few minutes the emanation, even at the temperature of liquid air, gradually diffuses, and the area of distribution becomes much larger. Ramsay has observed that the emanation condensed at the temperature of liquid air can be partly removed by continual pumping, indicating that it has an appreciable vapour-pressure at that temperature. This effect, however, becomes far more noticeable when using a pentane bath whose temperature is not more than  $10^{\circ}$  or  $20^{\circ}\text{C}.$  below the temperature of condensation. Every stroke of the pump then removes a not inconsiderable fraction of the total emanation. There is another effect observed which is very striking. Suppose that the nearly pure emanation contained in the U-tube is condensed over a small area by applying the liquid air only to the bottom of the U-tube. If the U-tube is then fully immersed in liquid air, in the course of about ten minutes it will be observed by the phosphorescence that the emanation is distributed throughout the tube, even though the U-tube is not connected with the pump. In addition, a part of the emanation has condensed above the level of the liquid air. Such experiments bring out clearly that the emanation has a sensible vapour-pressure far below the temperature of condensation. There is continual volatilization of the emanation in one part of the tube and condensation in another part.

I desire to thank Mr. T. Royds, M.Sc., who very kindly assisted me in many of these experiments.

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