ART. XIII.—*A Quantitative Determination of the Radium Emanation in the Atmosphere*; by GEORGE C. ASHMAN.

It was shown by Elster and Geitel* in 1902 that a negatively charged wire exposed for a few hours in the air receives a radio-active deposit similar in character to the quick-changing radium products. The first attempt to measure the amount of radio-active matter in the atmosphere was made by Eve† in 1905 in Montreal. The method used consisted in collecting the active deposit on a charged wire placed in a cylinder of known volume. The results were apparently not very satisfactory, since the estimated amount of pure radium necessary to keep the emanation constant in one cubic meter of air varied from 82×10^{-12} to 287×10^{-12} gram. The smaller value was obtained from a relatively small cylinder out of doors, the other from a large abandoned water tank indoors. The same higher value was reached by both cylinders indoors. Subsequent experiments by the same author‡ emphasized the objections to the active deposit method. The maximum values were sixteen times the minimum, and furthermore this method does not furnish direct proof of the presence of radium emanation. Eve has recently§ described a rather complicated new method of determining directly the amount of radium emanation in the atmosphere. This method depends upon the discovery made by Rutherford that radium emanation is readily absorbed by specially prepared cocoanut charcoal. The maximum values obtained by the absorption method were seven times the minimum, ranging from 18×10^{-12} to 127×10^{-12} gram of radium for each cubic meter of air, the probable average value being 80×10^{-12} . The well-known experiments of Rutherford and Soddy on the condensation of radium emanation suggested the possibility of a quantitative separation of the emanation from the atmosphere by means of liquid air. The qualitative separation was indeed accomplished in 1903 by Ebert.|| In my experiments, undertaken at the suggestion of Professor H. N. McCoy, air drawn from out of doors at ground level was passed through a purification train composed of KOH solution, H_2SO_4 , $CaCl_2$, and solid KOH, and then through a coil of copper tubing immersed in liquid air, and was finally collected in aspirators made of carboys of known capacity. The coil was made of copper tubing with an outside diameter of 3.2^{mm} and walls 0.5^{mm} in thickness. This was wound concentrically about an axis in such a way as to allow ample space between the turns so that every part of the coil would be completely bathed in the cooling liquid.

* Physik. Zeitschr., ii, 590, 1901.

† Phil. Mag., x, 98, 1905.

‡ Phil. Mag., xiv, 724, 1907.

§ Loc. cit.

|| Sitzb. Akad. Wiss. München, xxxiii, 133, 1903.

The entire coil occupied 75°C of space and could be easily kept submerged in liquid air in a small vessel. Two hundred liters of dry air, free from carbon dioxide, could be drawn through the coil at a moderate rate in six hours. At the end of that time the coil was allowed to heat up and the volatilized emanation was transferred to a standardized gas electroscope. This was made of an air-tight brass cylinder of about one liter capacity, supporting a gold-leaf system. This electroscope has been in use by Professor McCoy for more than two years and has a very small, almost constant natural leak of about 0.148 divisions per minute (whole scale 100 divisions), when exhausted and refilled with fresh dry air. The electroscope was standardized by the method described by McCoy and Ross,* which consisted in observing the rate of discharge caused by the emanation from a portion of a mineral containing a known amount of uranium. This activity observation was made just $3\frac{1}{4}$ hours after the separation of the emanation from the mineral and 3 hours after its introduction into the electroscope. The amount of radium associated with one gram of uranium in a mineral was taken as 3.4×10^{-7} .†

The results of four experiments calculated on the basis of the amount of radium necessary to maintain the emanation constant in one cubic meter of air are as follows:

(1)	86×10^{-12}	gram radium.
(2)	58×10^{-12}	“ “
(3)	45×10^{-12}	“ “
(4)	200×10^{-12}	“ “

These results seem to show a considerable variation in the amount of emanation in the air at different times; similar variations were found by Eve both by the excited activity method as well as by that in which the emanation was separated by means of charcoal. It was possible, however, that the variations in my results were due to incomplete condensation of the emanation. To decide this question, a second coil of tubing exactly like the one described above was joined to the first; both coils were immersed in liquid air, and purified outside air was run through the two coils in series at the same rate as in the four experiments above described. The emanation in the first coil corresponded to 51×10^{-12} gram of radium per cubic meter. *The second coil did not contain a trace of emanation.* This experiment clearly proved that the first coil condensed all the emanation in the air that passed through it, and showed conclusively that the observed variations were really due to variations in the amount of emanation in the air at different times. Such being the case, simultaneous duplicate determinations of the amount of radium emanation in the air

* J. Am. Ch. Soc., xxix, 1700, 1907. † Boltwood, this Jour., xxv, 296, 1908.

should yield identical results. Such duplicate determinations were carried out by dividing the air current which had passed through the purification train and passing each half through a separate coil. In this way equal volumes of air passed through the coils simultaneously under exactly similar conditions. When corrections for the lapse of time between the observations on the contents of the coils were made, it was found that each had collected emanation corresponding to 131×10^{-12} gram of radium. This furnished additional proof that the method can be relied upon for quantitative results. As a mean of all my experiments the amount of radium necessary to produce the observed amount of emanation per cubic meter of air is 96×10^{-12} , or nearly 10^{-10} gram. This is about 25 per cent higher than the mean value found by Eve by the charcoal absorption method. The difference may easily be due to the variations in the quantity measured. Neither method is, however, entirely above criticism. It seems that aside from the rather lengthy and complicated nature of Eve's experiments there are two possible sources of error. One is that Eve assumes in his calculations that increasing the amount of emanation in the air three- or fourfold by the introduction of a standard radium solution does not affect the fraction of the emanation absorbed by the charcoal. This has not been tested experimentally. The other is the fact, not taken into account, that the emanation is not completely removed from a radium solution by the bubbling method. The application of this correction, however, would reduce Eve's results to a still lower value. Perhaps some of the difference between our results may be accounted for by the fact that in Eve's experiments the air was taken at a level of the fourth floor of a building, while in the experiments described here the air was taken at the earth's level. In my own experiments the fact that the second coil, after the passage of the air through the first, did not contain an amount of emanation detectable by our electro-scope only proves that under the conditions of the experiment the first coil collected all the emanation capable of condensation at the temperature of liquid air. The complete condensation is limited only by the value of the vapor pressure of radium emanation at the temperature of liquid air. The experiment of Rutherford and Soddy* indicates that the vapor pressure below the condensation point is practically zero, while Ramsay† observed luminous bubbles passing down the walls of the vacuum tube while exhausting a vessel containing the frozen emanation. This would indicate an appreciable vapor pressure even at the temperature of liquid air.

The net results of all experiments show that the amount of

*Loc. cit.

†J. Chem. Soc., xci, 932, 1907.

emanation in the air varies between rather wide limits from time to time and notably with atmospheric conditions. The high value obtained in my fourth experiment is without doubt due to the fact that that determination was made immediately after a heavy rain and general thaw, following several weeks of freezing weather with an unusual covering of snow on the ground. Probably the accumulated emanation was suddenly liberated by the rapid melting of the snow and consequent softening of the earth's crust. It is of interest to note that experiment (5) was made during a prevailing high barometric pressure, and experiment (6) during a low pressure. The difference in the barometric readings on the two dates amounted to 20^{mm} of mercury. The other weather conditions were normal. A complete study was made of the activity curve of the emanation collected in experiment (4), which proved it to be identical with that of the radium emanation. The activity reached the maximum value in about three hours after introduction into the electroscope and decreased in the usual way to half value in about 3.5 days. This showed that the active material consisted only of radium emanation. The conditions of the experiment eliminated the possibility of introducing into the electroscope any thorium emanation which may have been condensed in the copper coil, since only a few minutes are required for thorium emanation to decay to a very small fraction of its initial value. The following table indicates the course of the activity curve of the emanation in experiment (4). The different times are placed in column (1), and in column (2) are the corresponding activities in scale divisions of the graduated eyepiece passed over by the gold-leaf per minute. The activities are corrected for the natural leak of the electroscope.

(1)	(2)
11 min. -----	761
60 " -----	852
126 " -----	963
180 " -----	1.100 max. activity.
19 hours -----	927
2 days -----	703
2.8 " -----	604
3.3 " -----	546
3.82 " -----	490

Conclusions.

The results of these experiments show that by cooling atmospheric air to the temperature of liquid air the radium emanation in it can be completely condensed and its amount accurately determined. Six measurements made at Chicago showed that the average amount of radium emanation per cubic meter of air could be maintained by 1.0×10^{-10} gram of radium.

Kent Chemical Laboratory, University of Chicago, May 20, 1908.