Art. XXVII.—*The Production of Radium from Uranium;* by Bertram B. Boltwood.

The hypothesis that radium is a disintegration product of uranium has been greatly strengthened through the demonstration of the fact that in radio-active minerals the quantity of radium is directly proportional to the quantity of uranium present.* On the basis of the disintegration theory a proportionality of this sort is to be expected between the parent element and its radio-active successor.

Additional data on this highly important question are however desirable, and a single experiment likely to further elucidate the problem has been independently undertaken by a number of different investigators. This experiment consists in observations conducted on a carefully purified uranium salt with a view to determining whether, with the lapse of time, measurable quantities of radium will be produced within it. If radium is a *direct* product of uranium through the intermediate stage of uranium-X and if the average life of radium is approximately 1,000 years, then it can readily be deduced that, with the delicate methods of measurement at command, the quantity of radium formed in a few hundred grams of uranium salt will be readily detectable and measureable after the lapse of a period no longer than a month. If, however, one or more transition products of a relatively slow rate of change intervene between the substance uranium-X and radium, the production of radium will be so protracted that no quantity of it sufficiently great to permit its detection will be formed within a greatly extended period.

The difficulties involved in the experimental demonstration of the growth of radium do not appear to be great. Uranium forms no radio-active, gaseous disintegration product, while the radium emanation affords a most convenient means of quantitatively estimating any radium which may be present. A solution of a carefully purified uranium salt can therefore be prepared and can be tested at intervals for radium emanation. If radium is formed from the uranium its existence will be indicated by the presence of radium emanation in the uranium solution.

Three papers in which an experiment of this character is described have been published by Mr. Soddy.† In the first

* Boltwood, Phil. Mag. (6), ix, 599; Strutt, Proc. Roy. Soc. Lond., lxxvi, 88; McCoy, Berichte d. deutsch. chem. Ges., xxxvii, 2641.

† "The Life-history of Radium," Nature, lxx, 30; "The Origin of Radium," Nature, lxxi, 294; "The Production of Radium from Uranium," Phil. Mag. (6), ix, 768. Mr. Whetham has also published two contributions on the same general topic (Nature, lxx, 5; *ibid.*, lxxi, 319) in which he states

paper, published May 12, 1904, very scanty details of the experimental procedure are given, but a summary of the conclusions reached at that time by the author is as follows:

1. The quantity of radium which has accumulated in one kilogram of uranium nitrate in twelve months is less than 10^{-11} gram.

2. The question so far as the production of radium *from uranium* is concerned is practically settled.

3. If uranium changes into radium, less than one ten-thousandth part of the theoretical quantity is produced during the first year's accumulation.

4. The evidence may be taken as indicating that uranium is not the parent element of radium.

The second paper, published Jan. 26, 1905, eighteen months from the commencement of the experiment, is likewise lacking in a detailed account of the experimental methods, but the author states that measurements carried out at that time with the kilogram of uranium nitrate under observation indicate that it contains $1{\cdot}5\times10^{-9}$ gram of radium, a quantity which, while of considerable relative magnitude, is only one five-hundredth of the amount to be expected from the disintegration theory on the assumption of a direct change. The author suggests that the greater part of the radium emanation may (under the conditions of the experiment) be retained in the uranium solution and not evolved as a gas. On the basis of the amount of radium assumed to be then present it is deduced that the fraction of uranium changing per year is 2×10^{-12}.

After pointing out certain sources of error likely to have exercised a disturbing influence during the elapsed period of observation, the author adds,—"if the whole series of measurements from the commencement are recalculated, eliminating the error alluded to, they are fairly consistent with there having been a steady production of radium at this rate continuously from the commencement." One of the sources of error alluded to was the introduction of very considerable quantities of radium salts into the laboratory during the period when the kilogram of uranium nitrate was under observation. It is stated that the presence of this radium greatly disturbed the electroscope in which the measurements were conducted. Additional difficulty had been previously experienced in attempting to standardize the measuring instrument with the emanation corresponding to a known weight of pure radium salt.

that he also believes that he has observed indications of the growth of radium in uranium compounds. Since Whetham's communications contain neither any account of experimental details nor any record of quantitative measurements, it is impossible to judge as to the value of the data on which the author's conclusion is based.

The third and more elaborate article by the same author appeared in the June number of the Philosophical Magazine. The data briefly given in the earlier articles are here treated at greater length and a closer insight can be gained of the experimental methods and the results on which the author's later conclusions are based. Although it is stated in this paper that observations had been taken occasionally over a period of eighteen months and that these observations indicated a *gradual* growth of the emanating power of the uranium solution, the only definite and directly comparable numbers are restricted to a total period of about three weeks (Dec. 17, 1904 to Jan. 9, 1905) and include only four measurements conducted at the close of the period of observation.

Without entering into a discussion of various minor details in Mr. Soddy's papers, it is desired to call particular attention to the following important considerations in relation to the experimental data submitted:

First. No conclusive evidence is brought forward to show definitely how much or how little radium was present in the uranium solution at the commencement of the experiment.*

Second. It appears extremely possible that the increase in the content of radium which Mr. Soddy believes he has observed in his uranium solution may in fact have been due to the accidental and unconscious introduction of radium salts during the tests conducted at the end of the twelve months period. According to his own statements these tests were carried out in a laboratory notably contaminated with various radio-active products, and the accidental introduction of the sub-microscopic quantity of material ($1{\cdot}6 \times 10^{-9}$ gram.) which was afterwards detected would account for the later positive results. The liability of contamination from an extraneous source is strongly suggested by the behavior of Mr. Soddy's electroscope, in which the normal air leak has risen from 0·048 division per minute to 1·56 division per minute, an increase of over thirty times, during the period covered by his experiments.

The conditions essential to the elucidation of the question of the actual production of radium in uranium compounds would seem to be:

* The writer of the present paper convinced himself at the beginning of his own experiments that the method of procedure followed by Mr. Soddy in testing his solutions for radium emanation is entirely unsuited for the determination in question. A concentrated solution of incompletely purified uranium nitrate containing traces of radium gave up only a fraction of the total radium emanation generated within it when the solution was allowed to stand for days in contact with a small air space and air was bubbled through it. It was speedily found that only by boiling the solution vigorously for about fifteen minutes could the total emanation present be positively separated.

(*a*) The employment of a method for the determination of radium which gives positive and quantitative results. The method must be suitable for the determination of very small quantities of radium and must be capable of indicating the *maximum* quantity present at all times.

(*b*) The preparation of a pure compound of uranium and the demonstration that the compound is initially free from radium.

(*c*) Proper conditions for testing and preserving the uranium salt in order to preclude the introduction of radium or radium emanation from external sources, so that if the presence of radium is noted it can be assumed with certainty that the radium found has actually been formed in the solution.

It would appear that none of these essential conditions has been fulfilled in the experiment described by Mr. Soddy.

The writer of the present paper has been conducting an experiment on the growth of radium in a uranium solution for the past thirteen months. The conditions of the experiment were the following: In May, 1904, a kilogram of "purest uranium nitrate" was purchased from Eimer & Amend of New York City. This material was tested qualitatively for radium (through the emanation) and readily detectable quantities of this element were found to be present. The salt was dissolved in distilled water and the solution was filtered. The compound was then recrystallized five separate times, the conditions being so chosen that the separate crystals of each of the different crops were not over two millimeters in cross-section. The mother liquors were each time removed from the crystals on a suction filter, and the crystals were washed with a small quantity of ice-cold water.

The final yield of purified material was a little in excess of 200 grams. Of this 100 grams were taken and dissolved in pure, distilled water. This solution was introduced into a glass bulb with a capacity of approximately 400^{cc}, diluted to about 250^{cc}, and the neck of the bulb was drawn out into a short capillary and sealed in the flame of the blowpipe. The solution was sealed up on July 8, 1904. Thirty days later the bulb was opened under conditions which precluded the escape of any portion of the contained gases and the entire gaseous contents were removed and transferred to an electroscope. In order to completely displace the dissolved gases and any radium emanation which might have been present the solution was boiled vigorously for about fifteen minutes.*

* The removal and collection of the gaseous contents of the bulb was accomplished by the use of the apparatus which has been described in a previous paper (this Journal, xviii, 379). The neck of the bulb containing the uranium solution having been first notched with a file, it was inserted in the rubber tube D, the point was broken off within the tube, and the gases displaced from the bulb on heating were collected in the burette D, which was filled at the start with boiling water.

The type of electroscope used in this investigation has already been described (this Journal, xviii, 97). The emanation from the radium associated with 0·1 gram of uranium in a radio-active mineral caused a leak of approximately 21 divisions per minute. Assuming that the 100 grams of uranium nitrate contained 48 grams of uranium, the leak corresponding to the quantity of radium in radio-active equilibrium with 48 grams of uranium would be approximately 10,000 divisions per minute. The normal air leak of the instrument was 0·012 division per minute, and an increase of 0·005 division per minute could have been detected with certainty. The electroscope was therefore capable of indicating the presence of a quantity of radium equal to 5×10^{-7} of the equilibrium quantity. The actual quantity of radium equivalent to a leak of 0·005 division per minute was $1{\cdot}7\times10^{-11}$ gram.*

On introducing the gases present† in the uranium solution into the electroscope *no increase* in the leak of the instrument could be detected although the observations were continued over a period of eight hours. The quantity of radium present at the start was therefore less than $1{\cdot}7\times10^{-11}$ gram.

The uranium solution in the bulb was allowed to cool, and the neck of the bulb was again sealed. At the end of six months from the start, in January, 1905, the uranium solution was again tested under conditions identical with those under which the first test was carried out. Entirely negative results were obtained and the quantity of radium then in the solution was still less than $1{\cdot}7\times10^{-11}$ gram. A similar test was conducted on August 2, 1905, 390 days from the commencement, and no evidence of the presence of radium emanation was even then obtained. It can therefore be positively stated on the basis of sound experimental data that in 390 days the quantity of radium formed from 48 grams of uranium in a uranium nitrate solution is less than $1{\cdot}7\times10^{-11}$ gram.

The quantity of radium which can have been produced in the given time is therefore less than one two-millionth of the equilibrium quantity and less than one sixteen-hundredth of the quantity which would be expected from the disintegration theory if the value of λ for radium is taken as $8{\cdot}8\times10^{-4}$ $(\text{year})^{-1}$.‡ The quantity is furthermore only about one-tenth of the quantity assumed by Mr. Soddy to have been formed from an equal quantity of uranium in his solution during an interval of eighteen months.

It is important to add that the whole series of measurements has been conducted in a laboratory which has been carefully

* Rutherford and Boltwood, this Journal, xx, 55.
† At the end of the 30-day period.
‡ Rutherford, Trans. Roy. Soc. London, (A) cciv, 215.

protected from contamination by the salts of radium or other radio-active substances, and that the electroscope used has been reserved for this particular research, its original normal air-leak having remained unaltered throughout the entire period. It has therefore been unnecessary to introduce any corrections or to make any allowances for possible errors due to known causes of any description.

The experiments described in this paper are considered to indicate that the results obtained by Mr. Soddy are without significance and that one or more products of a slow rate of change intervene between uranium and radium.

It is claimed, moreover, that the conclusions in Mr. Soddy's first paper, so far as they relate to the *direct* transformation of uranium into radium, are more truly in accord with the actual facts than are those contained in his later publications.

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