ART. XXXVIII.—*The Radio-activity of Thorium* ;* by
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It has been shown by O. Hahn† that it is possible to separate from thorianite minute quantities of a radio-active substance which is far more active than what is known as thorium. The fact that this substance gives off the same emanation as thorium has led him to suggest that the activity of thorium may be due to the presence in thorium of this substance, which he has named radio-thorium. He has further made the natural supposition that radio-thorium is a disintegration product of thorium. But so far as the writer knows, radio-thorium has not yet been separated from any source except thorianite and no quantitative determinations of the relation between the amount of thorium and its radio-activity has been made, so that the interesting suggestions mentioned above cannot be regarded as fully confirmed.

The following experiments were undertaken in order to determine the quantitative relation between the thorium activity of various minerals and separated salts, and their content of thorium.

The method used is based upon the measurement of the excited activity obtained by exposing a negatively charged body to the emanations evolved by the substance to be tested. The adjoining figure is a sketch of the charging vessels used in these experiments. Each mineral or salt to be tested was dissolved and the solution poured into a flat-bottomed glass dish, A, of 9.5^{cms} diameter and 4^{cms} depth. This was placed in a tin vessel, C, of 15^{cms} diameter and 18^{cms} height, which had a movable cover and could be made air-tight. The body upon which the active deposit was to be obtained was a circular copper plate, BB, of 11^{cms} diameter,

* Read before the American Physical Society, Feb. 24, 1906.

† Chemical News, April 28 and Dec. 21, 1905, *Jahrbuch für Radioaktivität und Elektronik*, 1905.

insulated from the tin vessel and connected to the negative terminal of a battery of 400 volts, the other terminal being connected to the tin vessel.

After exposures of 19 hours the copper plates were taken out of the charging vessels and introduced into a testing vessel connected with a Dolezalek electrometer, and the activity observed as usual. Another testing vessel, containing a uranium oxide standard, was connected with the electrometer, in parallel with the first testing vessel, in order to test the sensitiveness of the electrometer during the experiments and allow for changes in the sensitiveness if there were any. The electrometer had a sensitiveness of about 200^{cms} per volt with 100 volts on the needle and the scale at a distance one meter from the mirror.

The emanation generated at a given horizontal layer of the solution has to diffuse through the liquid above that layer in order to reach the surface. Therefore on account of the rapid decay of the thorium emanation (half-value period being 54 seconds) the percentage of the emanation, generated at that layer, which reaches the surface of the solution, will depend upon the depth of the layer. Thus the concentration being the same, the emanation which crosses a square centimeter of the surface per second depends upon the depth of the solution, provided it is not so deep that the emanation produced at the bottom has time enough to decay to a negligible value before reaching the surface, in which case it will be independent of the depth of the solution. The solutions used in these experiments were not deep enough to fulfill the above condition, therefore it was necessary to make all the solutions of the same depth. The equality of depth was realized by putting equal volumes (50^{cc}) of each solution in the flat-bottomed dishes, which were of the same diameter (9.5^{cms}). For similar reasons the negatively charged plates were kept at equal distances from the surface of the solution to which they were exposed.

The solutions tested were of different concentration, therefore in order to be able to compare their activities it was necessary to determine the quantitative relation between the concentration of the solution and the amount of emanation obtained. Two solutions of thorium nitrate were prepared, one of which had a concentration twice as great as the other. Equal volumes of these solutions were placed in flat-bottomed glass dishes of equal diameter, thus securing equal depths. Two copper plates were exposed to these solutions under similar experimental conditions and introduced into the testing vessel. The ionizations produced by the active deposits obtained from the more concentrated and the less concentrated

solutions were found to be 10.9 and 5.4 respectively. These results show that, everything else being the same, the amount of emanation obtained is strictly proportional to the concentration of the solution, as would be expected on theoretical grounds.

The substances tested, chosen on account of their easy solubility, and the results obtained are given in the following table:

Substance.	No. of grams in solution.	Percent- age of ThO ₂ .	No. of grams of ThO ₂ .	Observed activity.	Specific activity.
I.	II.	III.	IV.	V.	VI.
Thorite -----	2.00	51.7	1.034	{ 25.7 26.3	{ 24.8 25.4
Thorianite -----	1.29	76.5	0.987	{ 21.2 25.2	{ 21.5 25.5
Thor. nitrate (1) ..	2.20	45.6	1.003	10.7	10.7
“ “ (2) ..	2.15	46.6	1.002	12.5	12.5
“ “ (3)*. 1.00	1.00	38.0	0.38	4.3	11.3
“ “ (4) ..	0.77	48.9	0.376	8.3	22.1
“ “ (5) ..	2.07	48.3	1.00	22.0	22.0

Column I. The thorite was dissolved in dilute hydrochloric acid. The solution was evaporated to dryness, to render the silica insoluble, the silica filtered off and the filtrate diluted in 50^{cc} of distilled water. The thorianite was dissolved in concentrated nitric acid, the solution diluted and a slight residue of insoluble material filtered off. The solution was then evaporated to remove the excess of nitric acid and the remainder diluted to 50^{cc} with distilled water. The thorium nitrates number (1) and number (2) were prepared by the Welsbach Light Co., from North Carolina and Brazilian monazites respectively. Thorium nitrate number (3) was bought from Eimer & Amend about three years ago. Thorium nitrates number (4)† and number (5)† were prepared from North Carolina monazite and from thorianite respectively, by Dr. B. B. Boltwood, to whom the writer is indebted for the minerals and salts tested in these experiments, as well as for their chemical analyses.

Column II gives the number of grams of the substances in the solutions, column III the percentage of thorium oxide in each substance.

In column IV the number of grams of thorium oxide present in the solutions is given. It is obtained by multiplying the numbers of column II by those of column III.

* The percentage of ThO₂ of this salt was not known, therefore it was calculated from the formula Th(NO₃)₄ · 12H₂O. This gives the minimum percentage, hence the calculated specific activity is maximum.

† The process of preparation of these salts is given in a paper by Dr. B. B. Boltwood, in this number of the Journal.

Column V gives, in centimeters per minute,* the average of the ionization produced by the active-deposit measured between 4 and 5 hours after the removal of the potential difference from the negatively charged plate. Some of the substances tested contained more or less radium and actinium. Therefore a comparison of the activities observed during the first few hours, after the removal of the potential difference, could not have been a comparison of the activities due to thorium. But thanks to the rapid rates of decay of the excited activities due to radium and actinium compared with that due to thorium, the activities observed after 4 hours from the removal of the potential difference were entirely due to thorium, the part contributed by radium and actinium having become negligible. Two sets of observations were taken for thorite and thorianite, of which the second set was taken under more favorable experimental conditions. The average observed activities obtained from the first set were 25.7 for thorite and 21.2 for thorianite, while those obtained from the second set were 26.3 and 25.2 respectively.

In column VI the activity per gram of thorium oxide of each substance is given. It is obtained by dividing the numbers of column V by those of column IV. For brevity this will be called the specific thorium activity of the substance.

The agreement between the specific thorium activities of thorite and thorianite is striking, when the difference in nature and origin of these minerals and the experimental difficulties are taken into consideration. On the other hand, there is just as close an agreement among the specific thorium activities of the first three thorium nitrates in the table. Yet there is a marked difference between the specific activities of these two groups, the thorium in the salts being only about half as active as the thorium in the minerals. This difference could not be explained by possible experimental or accidental errors. It was to be accounted for in some other manner. At first it was assumed that thorium might be composed of two or more simple elements of which only one was undergoing radio-active disintegration and giving off the characteristic thorium emanation. According to this, the specific thorium activity will be different for different substances which do not have a quantity of the emanating component proportionate to their content of the remaining components. Thus the difference among the specific activities is accounted for, but the agreement, which is of greater significance, remains to be explained. On account of its improbability and insufficiency this assumption, with some others which will not be considered here, was abandoned in favor of another.

* The spontaneous ionization in the testing vessel was 0.45^{cms}.

According to this hypothesis radio-thorium is a disintegration product of thorium and the producer of thorium X. Thorium emanation being a radio-active product of thorium X, the amount given off by a substance is proportional to the quantity of thorium X present. For a substance in which thorium X and radio-thorium are in radio-active equilibrium, the quantity of thorium emanation given off will be proportional to the amount of both thorium X and radio-thorium but not necessarily to that of thorium present in the substance. If, however, all three, thorium, radio-thorium and thorium X, are in radio-active equilibrium, the proportionality will hold for each of them. All of the substances tested were in radio-active equilibrium as regards thorium X. Therefore the quantity of thorium emanation evolved by any of them should be proportional to the amount of radio-thorium only or to the amount of both radio-thorium and thorium present, according as the latter were or were not in radio-active equilibrium in the substance.

The experimental results given in the above tables follow as natural consequences of this hypothesis. Thus the amount of thorium emanation evolved by the solutions of the minerals should be proportional to their content of thorium as well as radio-thorium, as these are, in all probability, in radio-active equilibrium in the minerals. In other words, the specific thorium activity of the minerals should be the same. This was shown to be the case for the minerals tested, and thorium nitrate number (5), which was prepared from thorianite.

On the other hand, this hypothesis leads to the conclusion that the low specific thorium activity of the commercially prepared salts is due to the loss of part of the radio-thorium in the process of chemical preparation. Therefore, if thorium nitrate salts are prepared from minerals without losing any radio-thorium, their specific thorium activity should be the same as those of the minerals. In order to test this, thorium nitrate number (4) was prepared from 10 grams of North Carolina monazite. The specific thorium activity of this salt was found to be 22.1. This is about the same as the specific thorium activities of thorium nitrate number (5) and the minerals thorite and thorianite. But thorium nitrate number (1), which was prepared from the same mineral (North Carolina monazite), had a specific thorium activity of only 10.7.* The only rational explanation of this great difference in the activity of thorium obtained from the same mineral but by two different analytical methods, is the one just given.

Thus thorium and radio-thorium were in radio-active equilibrium in the specimens of North Carolina monazite from

* Dr. B. B. Boltwood tested these substances by a method described in a paper in this number of the Journal and arrived at similar results.

which thorium nitrates number (1) and number (4) were prepared. No appreciable amount of radio-thorium was lost in the preparation of thorium nitrate number (4). Therefore thorium and radio-thorium were in equilibrium in this salt. This accounts for the fact that its specific thorium activity was about the same as those of the minerals.

About half of the equilibrium quantity of the radio-thorium, on the other hand, must have been separated from thorium nitrate number (1) during the process of its chemical preparation. The few years' time which had elapsed between its preparation from the mineral and these experiments was too short for the thorium and radio-thorium, in the salt, to come into radio-active equilibrium, hence the low specific thorium activity.

The more important conclusions arrived at by the above experiments may be summed up as follows:

First. The amount of radio-thorium in minerals is proportional to the quantity of thorium present. Therefore radio-thorium is a transformation product of thorium.

Second. If thorium and its successive products radio-thorium and thorium X are in radio-active equilibrium in a substance, the amount of thorium emanation evolved by the substance is proportional to the quantity present of any and all of them.

Third. The difference in the specific thorium activities of substances which are in radio-active equilibrium with regard to thorium X, is due to the separation of some of the equilibrium amount of the radio-thorium from the substance.

Fourth. The fact that thorium nitrate number (3), which was prepared over three years ago, was notably deficient in radio-thorium, indicates that the rate of recovery and consequently the rate of decay of radio-thorium is very slow, and that the half-value period cannot be below two years.

In conclusion, I wish to express my hearty thanks to Professor H. A. Bunstead for suggesting these experiments and for the kind interest he has shown during the progress of the work.

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