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ART IX.—*On the Radio-Activity of Thorium Salts;* by BERTRAM B. BOLTWOOD.

MEASUREMENTS of the α-ray activities of a number of minerals containing thorium have been described in an earlier paper.* A measure of the ionization produced by known weights of the finely-powdered minerals in the form of thin films was obtained by introducing the films into an electroscope and determining the rate of leak of the charge in terms of the fall of the gold-leaf in scale divisions per minute. On dividing the rate of leak by the weight in grams of the mineral in the film a number was obtained expressing the specific activity (activity per gram) of the given mineral. The minerals examined contained uranium as well as thorium. The activity of one gram of uranium with its equilibrium amounts of disintegration products (actinium, radium, etc.) has been found to be a constant† which will be called the normal specific activity of the uranium-radium series. The value of this constant for the particular electroscope used was determined by measurements of the activity of certain minerals containing uranium and no thorium. Knowing the content of uranium and the constant for the normal specific activity of the uranium-radium series, it was possible to calculate for each of the thorium minerals that portion of the specific activity of the mineral which was due to the thorium and thorium products which it contained. Dividing this by the weight (in grams) of thorium contained in one gram of mineral, a number representing the activity per gram of thorium was

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* This Journal, xxi, 415, 1906.

† McCoy, Phil. Mag., ix, 176, 1906; Boltwood, loc. cit.

obtained. It was found that, within the limits of experimental error, the activity corresponding to one gram of thorium in a mineral was the same for the different minerals examined, which indicated that the activity of one gram of thorium with its equilibrium amounts of disintegration products—the normal specific activity of the thorium series, as it can be called—was a constant.

Measurements were also made of the activities of a number of specimens of thorium oxide which had been separated by chemical methods from the minerals and from certain thorium salts prepared by the Welsbach Company. The relative ionization produced by a known weight of each of these oxides in the form of a thin film was determined in the electroscope. The specific activity of the oxides prepared directly from the minerals was found to correspond to the normal specific activity of the thorium series found in the minerals. The activity of the oxides prepared from the Welsbach salt was, however, found to be much lower than the normal. These results led to the conclusion that the chemical process employed by the Welsbach Company was in some way peculiar since it apparently resulted in the separation of over one-half of the radiothorium corresponding to the thorium present.

The question of the radio-activity of thorium in minerals and salts has been examined also by Dr. Dadourian,* who employed a method based upon the measurement of the activity of the deposit obtained by exposing a negatively charged plate to the emanation evolved by a solution of the thorium salt or mineral. The results obtained by Dadourian and the writer were in close agreement and led to similar conclusions. Results of a similar character were also obtained by McCoy and Ross† and by Eve.‡

Among the salts examined by Dadourian were two specimens of thorium nitrate, the one prepared from North Carolina monazite and the other from Brazilian monazite, which had been supplied by the Welsbach Company to the writer nearly two years before. Mr. H. S. Miner, the chemist of the Welsbach Company, stated that the former salt was about two years old and the latter at least one year and a half old at the time they were sent to me. A third salt examined by Dadourian was a specimen of thorium nitrate which had been purchased from Eimer & Amend about three years before the time at which he tested it. It had, however, been used in the meantime by the writer for the preparation of thorium-X, that is, the original salt had been dissolved in water, the thorium had been precipitated as hydroxide with ammonia,

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* This Journal, xxi, 427, 1906. † Ibid., xxi, 433, 1906.
‡ Ibid., xxii, 477, 1906.

and the washed hydroxide had been reconverted into nitrate. In order to again obtain the solid salt the solution of the nitrate had been evaporated to dryness under conditions identical with those under which a considerable number of other salts have been prepared and which give a salt containing about forty-eight per cent of thorium oxide. The number given by Dadourian as expressing the specific activity of the thoria in this salt is therefore undoubtedly too high and the correct value would be about 9·0. The reason for this low value will appear later in this paper.

The specimen of Welsbach salt examined by the writer consisted of a kilogram of thorium nitrate made from North Carolina monazite and had been received about fifteen months before the time of my experiments.

The three Welsbach salts examined by Dadourian and the writer were therefore at least four years old, three and one-half years old and one and one-third years old, respectively. The oldest salt contained about forty per cent of the radiothorium in equilibrium with the thorium present and the youngest salt must have contained at least thirty per cent of its equilibrium amount of radiothorium. The difference in ages of these two salts was about three years and they had both been prepared from the same mineral by the same process. If radiothorium was a product formed directly from thorium it was obvious that its period of decay (recovery) could not be less than half-value in about six years and might be somewhat longer.

In April, 1906, the belief that the above data might have an important bearing in indicating the rate of disintegration of radiothorium was privately communicated to Dr. Otto Hahn, the discoverer of radiothorium. Dr. Hahn replied that the data supplied were difficult to reconcile with the results of his own experiments, made directly with a preparation of radiothorium, which seemed to show a half-value period of about two years for this substance. He made, however, at the same time the interesting suggestion that the lack of agreement could be explained if a rayless product having a slow rate of change intervened between thorium and radiothorium.

The rate of disintegration of radiothorium has since been determined by Blanc,* who finds that the half-value period is 737 days, and the existence of a product intermediate between thorium and radiothorium has recently been demonstrated by Hahn† in a very convincing manner.

Hahn made a careful examination of a series of samples of the intermediate chemical products obtained in the technical

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* Rend. della R. Accad. d. Lincei, xvi, 291, 1907.

† Berichte d. chem. Ges., xl, 1462, 1907.

preparation of pure thorium nitrate from monazite by the firm of Dr. O. Knöfler and Co., in Berlin. He found only insignificant differences in the specific activity of the thorium series in these samples and no differences indicating the separation of any considerable proportion of the radiothorium.*

On testing samples of the pure thorium nitrate which had been prepared by the same firm some years before, he found that these showed a conspicuously lower activity than the freshly prepared salts, and this decrease in activity appeared to continue for about three years, after which the activity remained fairly constant for some time. He also states that he has been able to obtain preparations which are free from thorium, but which show with the passage of time a marked increase in their activity and in their power to produce thorium emanation. These preparations must contain the intermediate product between thorium and radiothorium. He therefore reaches the conclusion that it is this intermediate product, for which he suggests the name "mesothorium," and not the radiothorium, which is separated from the thorium in the technical process of preparing pure thorium nitrate.

The films of thorium oxide which were originally used for the determination of the activities given in my earlier paper, and also a number of others which had been prepared and measured at the same time or shortly afterward, have been carefully preserved. The activity of these films has been recently re-measured in the larger of the two electroscopes described in the earlier paper and it has been possible to compare their present activities with their activities at the time of the first measurement. It was found that the specific activities of all the oxides has decreased by an amount equal to from 15 to 30 per cent. of their former values.

The results obtained are shown in the following table. In column I the decrease in the activity of each oxide is given in terms of its activity when first measured. In column II is given the approximate time which elapsed between the two measurements. In column III is given the decrease to be expected in the activity of each oxide if the activity had been falling at a rate corresponding to half-value in 737 days (the rate of decay of radiothorium). Oxides numbered 1 to 8 are the oxides given corresponding numbers in my earlier paper. Oxide No. 9 was prepared from thorianite by a chemical process differing only slightly from that used in preparing oxide No. 5. Oxides No. 10 and 11 were separated from certain

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* During the past year I have made an examination of similar chemical products kindly supplied by the Welsbach Company. The results obtained were similar to those obtained by Hahn, and no marked differences were noted in the thorium specific activity of the freshly prepared materials.

technical products supplied by the Welsbach Company and obtained by them in the process of preparing pure thorium nitrate from monazite.

Table.

Number	Source of oxide	I Decrease %	II Time days.	III Decrease calc.
1	Mantle dust	18	500	38%
2	Welsbach nitrate	32	489	38
3	“ “	15	347	28
4	“ “	22	365	30
5	Thorianite	30	489	38
6	“	26	428	34
7	Monazite	26	428	34
8	Miner's oxide	30	365	30
9	Thorianite	30	408	33
10	Welsbach residue No. 3	23	331	27
11	Welsbach residue No. 4	19	331	27

It will be noted that none of the oxides has lost its activity at a rate greater than that corresponding to a fall to half-value in 737 days, while most of the oxides have lost their activity at a lower rate. The behavior of the oxides indicates that at the time they were first measured they each contained much less mesothorium than the quantity in equilibrium with the thorium present. Oxides numbered 2, 5, 8, 9 and 10 in particular must have contained but a small proportion of their equilibrium amounts of mesothorium since the rate of fall of their activity has so closely approached that of radiothorium itself.

The results which have been obtained clearly indicate that the low specific activity of the thorium series in the salts prepared by the Welsbach Company can not be attributed to any special peculiarity in the chemical methods employed in the Welsbach works. It also appears that the chemical separation of thorium from mesothorium can be effected without difficulty by a variety of reactions.

A portion of the Welsbach nitrate from which the three oxides Nos. 2, 3 and 4 had been indirectly prepared has been preserved in its original crystalline form. A small amount of this nitrate was converted directly into oxide by ignition, and the specific activity of this oxide was determined a few days later. This was done shortly after the second series of measurements of the older oxides had been carried out. It was found that the specific activity of the thorium series in the original nitrate is now practically the same as it was at the time when the first series of measurements was made. The observation of this fact at once suggested the possibility that even the precipitation of thorium as hydroxide from a solution of the nitrate is effective in separating thorium from mesothorium, since this was the only treatment to which the thorium in oxide No. 2 had been subjected.

Over two years ago I had made some experiments with the object of obtaining a more definite knowledge of the chemical behavior of thorium-X. At that time a considerable number of thorium-X residues had been prepared by the well-known method of precipitating the thorium as hydroxide from a solution of the nitrate, filtering off and washing the hydroxide, evaporating the filtrate to dryness, and gently igniting the residue to remove the ammonium salts present. The amount of thorium nitrate used in some of these experiments was as much as a hundred grams and the volume of the filtrate was often more than two liters. In these experiments it was always found that the residue, after the removal of ammonium salts, contained very appreciable amounts of thorium. This thorium was finally removed from the residue by a second treatment with ammonia in a solution of small volume. A number of such thorium-free residues had been prepared and measurements of their activity had shown a steady fall for a period of about 30 days. After 30 days the residues still retained a definitely measurable activity, which was comparatively small, however, and amounted to a leak of only a few divisions per minute in the electroscope. This residual activity, which was observed further in some instances for a period of about one week, appeared to be fairly constant during that period, after which its progress was not further followed. It was attributed at the time to the presence of a little radium in the original nitrate.

Several of these old thorium-X residues have been preserved, and as soon as the possibility that they might have originally contained mesothorium suggested itself they were introduced into the electroscope and their activities noted. The activity of each of them was found to have risen enormously, until it has now reached a value which is many times greater than the minimum value to which it had originally fallen. These thorium-free residues, weighing together not more than a few milligrams, have now an activity equal to that of several grams of thorium oxide of normal activity and spontaneously evolve an emanation which is identical with that of thorium, falling to half-value in 54 seconds and producing the characteristic thorium-active deposit. These residues therefore contain radiothorium (and its products) which has been formed by the disintegration of the mesothorium originally present. If the half-value period of mesothorium is about 7 years, as suggested by Hahn, then these residues must still contain mesothorium and their activity will continue to increase for some time longer.

It is obvious, therefore, that the chemical process first described by Rutherford and Soddy for preparing thorium-X from thorium, consisting in the precipitation of the thorium as hydroxide from a solution of the nitrate, can be employed also for the separation of mesothorium from thorium. It has the advantage that the mesothorium is obtained in a relatively concentrated form, but it can be applied with advantage only where thorium nitrate of some age is available, since fresh thorium nitrate will contain little if any mesothorium.

The fact that the two oxides numbered 3 and 4, which were obtained through the intermediate formation of the normal and "basic" sulphates, respectively, also show a decrease in their activities is not in itself very suggestive, since in the preparation of the sulphates the nitrate was first converted into hydroxide. Also in the cases of the other oxides, No. 5 to No. 11 inclusive, the chemical operations through which the thorium passed from the first decomposition of the mineral to the final separation of the pure thorium salt were too complicated to make it possible to determine at what particular step the mesothorium was removed. From various data it appears probable, however, that the precipitation of thorium by sodium thiosulphate is effective in separating thorium from mesothorium.

A further point which appears to be worthy of notice in passing is the similarity in chemical behavior shown by thorium and radiothorium on the one hand, and by thorium-X and mesothorium on the other. We have no good evidence as yet of the chemical separation of thorium and radiothorium. These two elements appear to remain together most persistently through elaborate chemical operations which result in the separation of the thorium from every other known element. In contrast to this is the facility with which thorium-X and mesothorium can be separated from thorium and radiothorium. The chemical similarity of mesothorium and thorium-X is further indicated by what follows. Nearly two years ago an attempt was made to separate radiothorium from thorium by precipitating barium sulphate in a dilute solution of a thorium salt. This experiment was performed because it was thought that the entrainment of radiothorium by barium sulphate might explain the presence of radiothorium in the radium-barium sulphate residue for thorianite where Hahn had first obtained it. The precipitated barium sulphate was highly active when first prepared, but its activity fell regularly at a rate corresponding to half-value in 4 days, until at the end of about 40 days it had reached a negligible value. At the start it therefore contained thorium-X but no appreciable amount of radiothorium. This precipitate of barium sulphate has recently been examined and is now quite active. It gives off thorium emanation but contains no thorium. Its present activity is therefore due to radiothorium formed from the mesothorium which was precipitated with it. From this it seems probable that the radiothorium which Hahn separated from the residue of insoluble sulphates, obtained some time before in working up a considerable quantity of thorianite, had not been present in the residues when first prepared, but had been formed in them later through the disintegration of mesothorium. This supposition is further strengthened by Hahn's statement* that his radiothorium probably contained some mesothorium.

It appears quite likely, therefore, that the entraining action ot barium sulphate on mesothorium was directly responsible for the presence of radiothorium in the thorianite residues.

Summary.

Measurements of the changes which have taken place in the activity of certain thorium preparations have given results which are strongly in support of Hahn's assertion that an intermediate product having a slow rate of change and not emitting α-rays exists in the thorium series between thorium and radiothorium.

Certain methods for the separation of this intermediate product from thorium have been described.

Sloane Laboratory, Yale University,
New Haven, Conn., June 16, 1907.

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* Loc. cit.