

T H E

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

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ART. XXX.—*On the Radio-activity of Uranium Minerals;*
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[Contributions from the Sloane Physical Laboratory of Yale University.]

A COMPARISON of the radio-activity of uranium minerals with the radio-activity of freshly prepared uranium compounds and metallic uranium was first made by Madame Curie* and is of interest chiefly because it was one of the first steps which led to the discovery of polonium and radium. Further, and much more elaborate, experiments of a similar character have been carried out by McCoy, who has published a number of important papers on the subject. In McCoy's first paper† it is stated that the uranium minerals (free from thorium) have an activity which is 5.7 times as great as that of the uranium which is contained in them. In a subsequent paper the value of the ratio was found to be 4.15,‡ and in a recently published paper§ the value is given as 4.54. These differences in the value for the ratio are due to the introduction of certain modifications in the methods of analysis, measurement and calculation which were employed.

A knowledge of the exact value of this ratio is highly desirable and its determination is by no means a simple matter. It is also equally important that we should know what part of the total activity of a uranium mineral is due to each of the separate radio-elements or products which are contained in it. It was particularly with a view to obtaining light on the latter question, namely, the relative proportion of the total activity of uranium minerals due to each separate active constituent,

* S. Curie, C. R., cxxvi. 1101, 1898.

† Ber. d. chem. Ges., xxxvii. 2641, 1904.

‡ Phil. Mag., xi. 176, 1906.

§ McCoy and Ross, Jour. Am. Chem. Soc., xxvii. 1698, 1907.

that the experiments to be described in this paper were undertaken.

The problem was first brought to my attention in April, 1905, by Professor Rutherford, who suggested that an attempt be made to determine the relative activity due to actinium and its known products in a uranium mineral. At his suggestion certain experiments were undertaken with the object of measuring the rise with the time in the activity of a uranium mineral from which the radium emanation and its immediate products (radium A, radium B and radium C) had been completely removed, and also of determining the relative activities of the radium and actinium emanations which were evolved by a solution containing a known amount of a uranium mineral.

In the former experiments a fraction of a gram of a pure uraninite was dissolved in dilute nitric acid and the solution was boiled to expel the radium emanation. The solution was heated for a further period of several hours, and was finally transferred to a shallow dish and evaporated to dryness. The radium emanation and the products of rapid change formed from it (RaA, RaB and RaC) having been completely removed in this manner, the dish with the residue was placed in an electroscope and the activity measured. The rise in the activity with the time due to the accumulation of fresh quantities of emanation and active products was then observed and the final maximum activity attained at the end of about thirty days was ultimately determined. Results were obtained which indicated that the activity of the residue free from radium emanation, radium A, B and C, was from 0.55 to 0.62 that of the residue when the maximum amounts of emanation and products were present. From these data and from other data on the relative activity of uranium minerals and the uranium contained in them, it was possible to calculate roughly the activity of the radium and known radium products as compared with the activity of the other active substances (including the actinium products) present in the mineral. The relative activity of the actinium products as calculated in this manner was found to be so low that it appeared highly improbable that actinium was an intermediate product in the main line of descent in the uranium-radium disintegration series.* This matter had been discussed in some detail by Rutherford.†

In the experiments in which it was attempted to measure the actinium emanation evolved by a solution of the mineral, it was found that the amount of the emanation given out by a

* Rutherford and Boltwood, this Journal, xx, 56, 1905.

† Radioactive Transformations, p. 177.

solution* containing as much as ten grams of a pure, soluble uraninite was too small to be measured or even to be detected with certainty. This result could be explained neither by the fact that the life of the actinium emanation was too short (3.9 seconds) nor on the assumption that the amount produced was too small, since certain dry preparations obtained from smaller quantities of the mineral and introduced in place of the solution gave out amounts of actinium emanation which could be readily measured. It appeared to be due rather to a very marked retention of the emanation by the solution, the real cause of which has not yet been discovered. It was evident, however, that no reliable data as to the relative amounts of radium and actinium present could be obtained by this method.

Considerable time was spent in testing the method depending on the measurement of the rise of the activity of the residues obtained from the solutions of the mineral, and the conclusion was finally reached that this was capable at best of giving but very rough approximations for the values of the relative activities. Efforts were then made to devise experiments by which more direct and accurate values could be obtained.

The important discovery by Bragg and Kleeman† that radium and its immediate products (radium emanation, radium A and radium C) emitted α particles with different ranges and velocities, did not seem to justify the earlier assumption made by Rutherford‡ that each change which gave rise to α rays supplied about an equal fraction of the total activity, and made a further experimental investigation of this matter very desirable. This was undertaken and the results obtained have been already published.§ It was found that the relative activities of the different products were approximately proportional to the ranges of the α particles emitted by each product.

It soon became apparent that the uranium minerals (namely, the primary uraninites) which were most suitable in all other respects to the purposes of the investigation, contained small proportions of thorium. The primary activity of thorium was still in question and the statements made by Hofmann, Zerban, Baskerville and others suggested that thorium might not be a radio-active element. It therefore became necessary to investigate this matter also before any definite conclusions could be drawn from the activities of the minerals. The careful examination of a considerable number of minerals contain-

* A strong current of air was drawn through the solution into a small electroscope.

† Phil. Mag., x, 318, 1905.

‡ Radio-activity, 1st edition, p. 308.

§ Boltwood, this Journal, xxi, 409, 1906.

ing varying proportions of thorium and uranium demonstrated that the specific activity of the thorium and its products in a mineral is constant* and furnished reliable data by which the activity of a uranium mineral could be so corrected as to eliminate that fraction of the total activity which was due to the thorium contained in it. The conclusions with regard to thorium were independently confirmed by Dadourian,† by McCoy and Ross‡ and by Eve.§

The experiments described in this paper were begun over two and one half years ago and have been steadily continued throughout the intervening period. Various improvements and modifications have suggested themselves from time to time and much of the work has been frequently repeated in order to insure greater accuracy and reliability. The results are even now by no means so satisfactory as could be desired and the repetition of some of the work would undoubtedly lead to more trustworthy values. It is believed, however, that the values as found are sufficiently accurate to permit certain important deductions and conclusions to be drawn from them.

It is of interest to note that the methods which were employed in several cases depended on the quantitative chemical separation of a number of the radio-elements from the complex mixture of active substances present in the mineral. Information as to the exact chemical behavior of the radio-elements other than uranium and thorium which can be found in the literature is extremely meager and, as will be pointed out later, is frequently untrustworthy. It has therefore been necessary not only to work out the methods of separation which were used, but to demonstrate that the separations were more or less complete by confirmatory evidence of a purely physical character.

The Radio-active Measurements.

The measurements of the radio-activity of the different minerals and preparations were made in an electroscope, a plan of which in vertical cross-section is shown in fig. 1. The ionization chamber was 14^{cm} in height, 19^{cm} in diameter at the middle and 15^{cm} in diameter at the top and bottom. It was made from two tin pans loosely fastened together by a single copper rivet which permitted the lower pan to be swung to one side for the introduction of the preparation to be measured. The preparations were placed on the bottom of the lower pan and the two sections of the ionization chamber were firmly

* Boltwood, this Journal, xxi, 415, 1906.

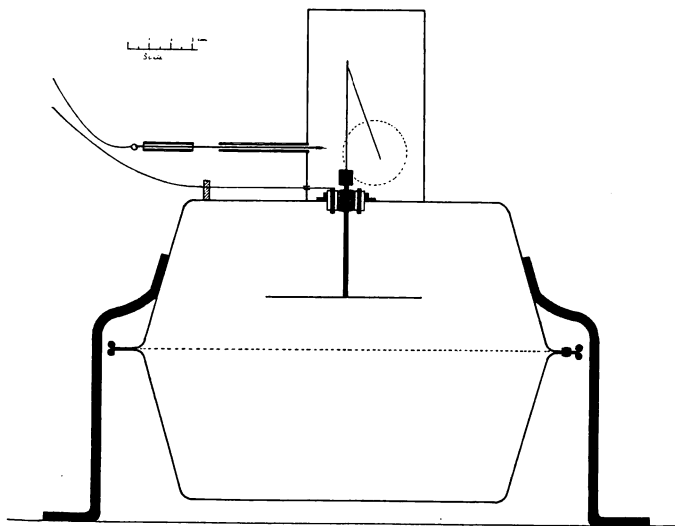
† This Journal, xxi, 427, 1906.

§ Ibid., xxii, 477, 1906.

‡ Ibid., xxi, 433, 1906.

held together by a spring clamp after the lower half had been swung back into position. The charged electrode was a circular aluminium plate 7.5^{cm} in diameter and was 9.5^{cm} from the bottom of the chamber. The vertical brass rod holding the electrode passed through a sealing-wax plug in the top of the chamber and carried on its top a brass plate and gold-leaf five centimeters in length and eight millimeters in width. The insulating sealing-wax plug was surrounded by a brass

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guard-ring which was kept permanently attached to the charging battery, consisting of 190 small storage cells. The gold-leaf was protected by a metal case with small mica-covered windows. The insulated electrode could be charged at will by touching the back of the plate carrying the gold-leaf with a fine wire inserted through a short glass tube in the side of the metal case. The guard ring and charging wire were connected through a water resistance with the negative terminal of the charging battery. The positive pole of the battery and the case of the electroscope were connected to earth. The movement of the gold-leaf was observed through a microscope rigidly mounted in front of the electroscope. The type of microscope used has already been described* and the practice was always followed of noting the time required for the passage of the

* This Journal, xviii, 99, 1904.

gold-leaf over a certain definite portion (8.0 divisions) of the scale in the eye-piece. The natural air-leak of the electroscope was low and averaged about 0.04 division per minute. The maximum and minimum noted in the course of over two years were 0.058 and 0.029 div., respectively. The air-leak was always higher in winter, when the windows of the laboratory were closed, than in summer, when the windows were open. With proper precautions the natural leak could be kept constant within a few per cent for days at a time. In every series of measurements the sensitiveness of the electroscope was determined by measurements of the leak produced by a certain standard film of uranium oxide. This film was attached to a plate of aluminium in a manner which will be described later. This standard film was carefully preserved during the entire course of the investigation. When the electroscope and reading microscope were undisturbed the sensitiveness of the electroscope remained quite constant for long periods, but during the time occupied by the experiments it was necessary on one occasion to completely dismount and re-assemble the entire apparatus. On several other occasions a slight readjustment of the microscope was made. These alterations produced slight changes in the constants of the instrument, which could be readily determined by the measurements of the standard film mentioned above. By means of these readings obtained with the standard film the different measurements can all be calculated in terms of a single standard. The results of earlier measurements as given in this paper have thus been reduced to the terms of the present sensitiveness of the instrument.

Preparation of the Films.—The method followed in preparing the minerals and solid preparations for the radio-active measurements has been described in an earlier paper.* The material to be tested was ground to an impalpable powder in an agate mortar with freshly distilled chloroform. At the end of the grinding operation the mixture of solid and chloroform consisted of a thin paste. A small amount of this paste was removed on the point of a small camel's-hair brush,† a little fresh chloroform was dropped on the brush, and the material was quickly and quite evenly spread over the surface of a sheet of aluminium 7.5^{cm} wide, 9^{cm} long and 0.1^{mm} in thickness. The aluminium sheets weighed about 2 grams, and the weight of the film of solid remaining after the chloroform had evaporated could be determined with considerable accuracy. The material adhered quite firmly to the surface of the plate and showed

* The Radio-activity of Thorium Minerals and Salts, this Journal, xxi, 418, 1906.

† The brushes before use were carefully cleaned with chloroform in order to remove any soluble substances contained in them.

no tendency to fall off even when the plate was completely inverted.

In measurements of a similar character to those here described McCoy* has used films of such appreciable thickness that a correction had to be made for the absorption of the radiations in the material itself. By using very thin films the absorption becomes inappreciable and the activity is directly proportional to the weight of the material present. This relation is indicated in the following table (Table I) giving the results of the measurements of a series of films prepared from an oxide of uranium containing 82.1 per cent of uranium:

TABLE I.

Film No.	Weight of oxide grams	Activity : Divisions per minute	Activity Weight
1	0.0324	3.16	98
2	0.0131	1.36	104
3	0.0087	0.885	102
4	0.0088	0.889	101
5	0.00435	0.446	102

In the case of the uranium minerals the absorption with increasing thickness of the film is more apparent, as is indicated in the following table (Table II):

TABLE II.

Film No.	Weight grams	Activity : Divisions per minute	Activity Weight
1	0.0364	13.76	378
2	0.0250	9.56	382
3	0.0229	9.11	397
4	0.0049	2.07	422

The results given in Table II are shown graphically in fig. 2, in which the ordinates are proportional to the activity and the abscissæ to the weights. The dotted straight line is drawn through the first point and the origin and indicates the locus of the points if no absorption took place. It is evident that for films weighing about 5 milligrams (and approximately 60^{cm} in area) the absorption of the radiations in the material of the film is very slight. The films of minerals used in these experiments weighed in no case more than 11 milligrams and no corrections were therefore made in the activities for any absorption of the radiations in the films themselves.

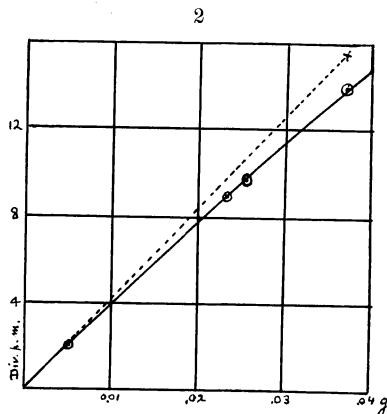
Determination of the Uranium in the Minerals.

An accurate determination of the proportion of uranium contained in the minerals was highly essential as it was desired to express the activity of all the other substances in terms of

* Jour. Am. Chem. Soc., xxvii, 391, 1905.

the activity of uranium taken as a standard. In my earlier work* I had found that very satisfactory results could be obtained when the uranium was separated and weighed as the phosphate, but in the present instance it was considered preferable to weigh the separated uranium in the form of uranoso-uranic oxide (U_3O_8) and to employ as a standard of radio-activity a specimen of the same oxide prepared in an identical manner from a very pure sample of uranium nitrate.

The method used for separating the uranium from the minerals was a slight modification of the method described by



Hillebrand.† One gram of the finely powdered mineral was decomposed with dilute nitric acid and the solution was evaporated to dryness. The residue was moistened with a little dilute nitric acid, digested with a few cubic centimeters of water and the resulting solution was filtered to remove insoluble matter. After further dilution the solution was treated with an excess of hydrogen sulphide and the precipitate of sulphides was filtered off.‡ The filtrate was then evaporated to dryness and the residue was heated for some time at 110° to insure complete drying. The dry residue was thoroughly extracted with pure, dry ether which removed nearly all of the uranium salt present. The material insoluble in ether was dissolved in dilute nitric acid, and to this solution an excess of

* Phil. Mag., ix, 603, 1905.

† Bulletin U. S. Geological Survey, No. 78, p. 46, 1891.

‡ It was found that when the precipitation was conducted in a very dilute nitric acid solution the precipitate could be filtered off and completely washed without the slightest difficulty. When a dilute hydrochloric acid solution was used the precipitated sulphides could not be satisfactorily removed as they ran through the finest filter paper with great readiness.

oxalic acid was added and the mixture was allowed to stand for 24 hours. The rare earths present together with a little calcium were precipitated as oxalates. The filtrate from the oxalates was evaporated to dryness and cautiously heated to destroy the oxalic acid present. The residue remaining was dissolved in a small amount of dilute nitric acid and this solution was poured into a cold solution of about 1 gram of ammonium carbonate in 20^{cc} of water. To this mixture a little hydrogen sulphide was added. It was then heated to boiling, allowed to cool and filtered. The filtrate was boiled to remove the ammonium carbonate present, made slightly acid with nitric acid, and added to the residue obtained by the evaporation of the ether solution. The uranium solution was then transferred to a standard volumetric flask and diluted to exactly 100^{cc}. Separate portions of this solution 10^{cc} in volume were measured out with a standard pipette. The uranium was determined in these portions in the following manner:—The solution was diluted to about 50^{cc}, and 10^{cc} of a freshly prepared solution of pure yellow ammonium sulphide was added.* The mixture was heated nearly to boiling for an hour, and the separated uranous oxide was filtered off and washed with hot water. After drying, the filter paper and precipitate were ignited in a porcelain crucible, at first gently in the air and finally at the highest heat of the blast-lamp in an atmosphere of oxygen. After determining the weight of the uranoso-uranic oxide obtained in this manner it was in many cases converted into the uranous oxide by a similar, intense ignition in an atmosphere of hydrogen,† and the weight of the uranium when in the form of the lower oxide determined. Very good agreement was shown by the results obtained in this manner.

Determination of the Thorium.—The determination of the thorium in the minerals was made by separating the thorium from the precipitate of rare earths thrown down by oxalic acid in the solution of the residue remaining after extracting the dry nitrates with ether. The oxalates were converted into oxides, the oxides dissolved by fusion with sodium bisulphate and subsequent treatment with water, and the thorium removed by making use of the solubility of thorium oxalate in an excess of ammonium oxalate.‡ In some cases the determination of the thorium was also carried out by other standard

* Remelé, *Zeitschr. f. anal. Chem.*, iv, 379, 1865.

† In the various works on analytical chemistry which I have consulted sufficient emphasis is not placed on the importance of highly heating both the uranoso-uranic and the uranous oxide. A very high temperature is essential in order to insure the complete conversion of either form of the oxide into the other.

‡ This Journal, xxi, 416, 1906.

methods, and the results of all determinations were in good agreement.

Preparation of the Uranium Standard.

The uranoso-uranic oxide used as a standard of the uranium activity was made from some very pure uranium nitrate which was a portion of that prepared some years ago for experiments on the growth of radium in uranium compounds.* A fraction of a gram of this nitrate was dissolved in 50^{cc} of water, an excess of a solution of pure, yellow ammonium sulphide was added, and the mixture was digested for an hour at the temperature of boiling water. The uranous oxide formed was filtered off and ignited over the blast-lamp in oxygen. After the weight of the uranoso-uranic oxide had been determined it was again ignited, this time in hydrogen, and converted into the uranous oxide. After weighing the uranous oxide this was again converted into uranoso-uranic oxide and again weighed. The weight of the U_3O_8 in both cases was the same and was in perfect agreement with the weight obtained for the uranous oxide. It was therefore assumed that the uranoso-uranic oxide finally obtained was pure and this material was used in preparing the standard. Two films of this material on aluminium sheets were made. The following table (Table III) gives the data obtained from their measurement.

TABLE III.

Film No.	Weight U_3O_8 g.	Activity div. per min.	Activity Weight	Activity per g. Uranium
50	0.0061	0.641	105	124 div. per min.
51	0.0063	0.663	105	124 " " "

In calculating the activity of one gram of uranium it was assumed that the oxide (U_3O_8) contained 84.8 per cent of uranium.

At the beginning of the investigation some uranium oxide supposed at that time to be pure U_3O_8 was prepared by igniting pure uranium oxalate first in air and then in oxygen at the highest temperature attainable with an ordinary Bunsen burner. This was the oxide used in the preparation of the films included in Table I. A duplicate sample of this oxide was preserved and when examined later it was found to contain only 82.1 per cent of uranium. Film No. 3 of this series was the film used throughout the investigation for determining the sensitiveness of the electroscope.

The Activity of the Minerals.

In attempting to reach any definite conclusions from data derived from the measurement of the activity of a uranium

* This Journal, xx, 239, 1905.

mineral one important point must be taken into consideration. This is the spontaneous loss of radium emanation from the powdered material, to which attention was first called by the writer.* It will be shown later that the activity due to the radium emanation and its immediate disintegration products is a considerable factor in the total activity of the mineral. In order to obtain a true measure of the activity of a mineral a determination must be made of the emanating power of the mineral in the form used in the film, and if the proportion of emanation lost is appreciable a correction must be made in the activity as measured.†

The proportion of the total emanation lost by the powdered minerals was determined in the manner previously described,‡ and the material used was the finely powdered mineral left after the evaporation of the chloroform with which it had been mixed in the operation of grinding. The necessity of any very appreciable correction for the emanation lost was avoided in at least one instance, by the use of a specimen of a very dense and pure uraninite (the Branchville material), in which the emanation lost by the powder was only 1.4 per cent of the total amount present. The data from which the correction for the emanation lost was calculated will be given later (p. 283).

The correction to be applied for the thorium contained in the mineral was determined in the following manner. A film was prepared from a specimen of thorite containing 52.0 per cent of thorium oxide and 0.37 per cent of uranium. The weight of mineral in the film was 0.00955 gram and its activity was 0.704 divisions per minute. This was equivalent to 73.7 div. per min. per gram of mineral. The activity due to the uranium would be equal to 2.2 div. per gram of mineral (576×0.0037). One gram of mineral contained 0.520 gram of thorium oxide, and the activity per gram of thorium oxide was therefore $71.5 \div 0.52 = 137$ divisions per minute in the electroscope.§

The following minerals were used in the experiments:—

No. 1. Uraninite from Branchville, Conn. This specimen was a portion of some very fine material which was most kindly presented to me by the late Professor S. L. Penfield, Curator of the Brush collection. It consisted of small, imperfect crystals

* Phil. Mag., ix, 603, 1905.

† This point was neglected by McCoy in his earlier experiments, but the method of determining and applying the correction was called to his attention by the writer. The correction has been applied in the paper which he recently published (Jour. Am. Chem. Soc., December, 1907).

‡ Phil. Mag., ix, 603, 1905.

§ This is equivalent to 156 div. per min. per gram of thorium. The activity of one gram of uranium was 124 div. per min. The ratio of these numbers is 1.26; viz., the specific activity of thorium containing equilibrium amounts of products is 1.26 times that of uranium. The value found by McCoy and Ross for this ratio is 1.27 (Jour. Am. Chem. Soc., xxix, 1709, 1907).

in a feldspar matrix from which they could be readily separated. The large specimen was crushed and about three grams of the pure uraninite was picked out. This was divided into two portions consisting of larger and smaller fragments respectively. Examined with a lens, the portion consisting of smaller fragments appeared to carry a slight admixture of the matrix. The appearance of all of the material indicated the complete absence of secondary alteration. The smaller fragments were taken for the preparation of this sample, which was found to contain 0.50 per cent of silica and matter insoluble in dilute nitric acid.

No. 2. This was prepared from the larger fragments mentioned above. It was found to contain 0.34 per cent of silica and matter insoluble in dilute nitric acid.

No. 3. Uraninite from Spruce Pine, N. C. This was a portion of a lot of about 50 grams of very pure material obtained from the centers of a number of good-sized lumps which had been externally altered into gummite and uranophane. The material selected showed only the slightest traces of secondary alteration and was found to contain only 0.03 per cent of material other than silica which was insoluble in dilute nitric acid. The silica present was equal to 0.14 per cent.

No. 4. Material similar to No. 3, but containing a slightly greater proportion of secondary alteration products. It contained 0.37 per cent of silica and 0.04 per cent of insoluble matter other than silica.

No. 5. Uraninite from Joachimsthal. Carefully selected material of fair purity, but containing small amounts of sulphides.

No. 6. Uraninite from Saxony. An inferior variety containing various impurities.

No. 7. Uraninite from Colorado. This material was very kindly sent to me by Professor McCoy, who stated that it was similar to the No. 1 Pitchblende from Colorado described in his paper in the *Philosophical Magazine* for January, 1906.

No. 8. Carnotite from Colorado. This was also obtained from Professor McCoy and was a sample of the No. 5 Carnotite mentioned in his paper. Both this specimen and No. 7 above were tested in the powdered form in which they were received.

No. 9. Carnotite from Colorado. Obtained through the kindness of Mr. William Zowe of Uranium, Colorado. It gave a residue insoluble in nitric acid amounting to 16.7 per cent of the total.

No. 10. Thorianite, Sabaragamuwa Province, Ceylon. A portion of some very fine material kindly supplied by Mr. H. S. Miner of the Welsbach Company.

The result of the measurements made with these minerals are given in Table IV.

TABLE IV.

No.	Mineral	Uranium Per cent	Thorium oxide Per cent	Weight of film	Activity of film Div. per min.	Activity per gram mineral	Activity due to ThO ₂	Activity due to uranium	Ratio of activity per gram uranium to act. of 1 g. U	Proportion of total emanation lost by powdered mineral	Correc- tion for emanation lost	Corrected ratio mineral uranium
1.	Uraninite, Branchville, Conn.	77.2	6.0	0.0060 g.	2.73	4.55	8	447	579	4.67	1.4%	4.70
2.	Uraninite, Branchville, Conn.	77.7	6.1	0.0111 "	5.03	4.54	8	446	574	4.68	2.2	4.68
3.	Uraninite, Spruce Pine, N. C.	78.5	1.9	0.0056 "	2.41	4.29	3	426	543	4.38	14.1	4.67
4.	Uraninite, Spruce Pine, N. C.	73.8	1.9	0.0049 "	2.07	4.22	3	419	551	4.44	14.0	4.73
5.	Uraninite, Joachimsthal	66.7	0.0	0.0047 "	1.76	3.76	0	376	564	4.55	6.2	4.68
6.	Uraninite,* Saxony	46.0	0.0	0.0057 "	1.49	2.61	0	261	568	4.58	3.0	4.64
7.	Uraninite,* Colorado	56.9	0.0	0.0040 "	1.22	3.05	0	305	536	4.32	13.3	4.60
8.	Carnotite,* Colo.	49.0	0.0	0.0055 "	1.21	2.20	0	220	449	3.62	33.6	4.32
9.	Carnotite,* Colo.	43.1	0.0	0.0066 "	1.50	2.27	0	227	527	4.25	12.0	4.50
10.	Thorianite, Ceylon	12.5	78.8	0.0061 "	1.11	1.82	109	73	584	4.70	1.0	4.72

* In specimens Nos. 6, 7, 8 and 9 the proportion of uranium contained in the minerals was not determined by direct analysis, but was calculated from the relative amounts of radium emanation from these and from the analyzed specimens.

The low values obtained for the activities of the carnotite specimens are not difficult to explain. This mineral is extremely porous and in its natural (unpowdered) state loses a considerable proportion of its radium emanation. It occurs, moreover, in an extremely permeable sandstone, is obtained from shallow excavations, and is subject to the action of percolating surface waters. It is therefore unsuited for the purposes of an accurate determination.

The average value of the ratios obtained from the first four specimens is 4.69, a number differing by less than 4 per cent from the value of the same ratio as determined by McCoy and Ross. The results may be taken as indicating that the activity of a uranium mineral containing its equilibrium amount of emanation is about 4.7 times the activity of the uranium which is present in the mineral.*

Relative Activity of Radium and Uranium in Minerals.

A solution was prepared by dissolving a few milligrams of recrystallized radium-barium chloride in 250^{cc} of distilled water containing a little free hydrochloric acid.† The emanation produced by a portion of this solution was compared with the emanation produced by a standard solution of radium bromide.‡ The amount of the radium in one cubic centimeter of the chloride solution was thus found to be 8.5×10^{-10} gram. By a comparison of the emanation formed in 10^{cc} of this solution with the emanation produced in known amounts of the analyzed uraninites (Nos. 1, 2, 3, 4 and 5, Table IV) it was determined that the radium in 10^{cc} of the chloride solution was equal in amount to that associated with 0.0250 gram of uranium in the minerals.

Portions of this solution 10^{cc} in volume were evaporated to dryness in shallow glass dishes under conditions which insured the complete removal of radium emanation and its immediate active products. The activity of the residue remaining in the form of a very thin film was then determined in the electro-scope.

The following values were obtained for the activities :

1.396, 1.373, 1.437, 1.341 ; average 1.386 div. per min.

The activity of 0.0250 g. of pure uranium was equal to $124 \times 0.25 = 3.10$ div. per min.

$$\frac{1.386}{3.10} = 0.447$$

namely, the activity of the radium itself in the minerals was 0.447 that of the uranium present.

Because of the variation shown in the separate results above given, and particularly because of a slight uncertainty as to the effect of the sides§ and non-conducting material of the glass

* In a communication published in *Nature* for January 3, 1907, the value 5.3 was given for this ratio. This high and incorrect value was obtained under the erroneous assumption that the substance obtained by moderately heating the oxide of uranium in oxygen was pure U_3O_8 .

† For further details concerning the preparation of this solution see this *Journal*, xxi, 410, 1906.

‡ Rutherford and Boltwood, this *Journal*, xxii, 2, 1906.

§ 9^{mm} in height.

dishes, a further experiment was made in which 10°C of the radium solution were evaporated to dryness in a shallow platinum tray 5^{cm} square with edges having a height of only 1^{mm} . The activity of the film obtained (the film extended to, but did not touch the edges) was 1.401 div. per min. This gave the value of the ratio as 0.451 .

It has been shown* that for the electroscope used in these experiments, the activity of radium containing equilibrium amounts of the emanation and the products radium A, radium B and radium C, is about 5.64 times the activity of the radium itself. Taking the activity of the radium in the minerals as 0.45 of that of the uranium present, the activity of the radium and its immediate products is found to be $5.64 \times 0.45 = 2.54$ times the activity of the uranium present. The activity of the equilibrium amounts of the products radium emanation, radium A, radium B and radium C is therefore equal to $4.64 \times 0.45 = 2.09$ times the activity of the uranium. This is the factor used in Table IV in correcting the activity of each mineral for the radium emanation lost by the powdered material.

An attempt was made to determine the activity of the products A, B and C by direct experiment. The radium emanation from exactly 0.200 gram of uraninite No. 4 (Table IV) was collected and introduced into an air-tight, glass vessel having a capacity of about 250°C . One end of the vessel consisted of a copper plate 8^{cm} in diameter, and 5.5^{cm} from this and near the opposite side was a spiral of copper wire. The copper plate was attached to the negative pole of a battery giving a potential of 400 volts and the wire spiral was connected with the positive terminal. At the end of about four hours the copper plate was removed and quickly placed in the electroscope. Its activity was followed for the course of about sixty minutes. As was to be expected, it was found that the amount of active deposit collected by the plate varied with the character of the field, and was greatest when the inner side of the glass vessel was entirely covered with a conducting coating to within about one millimeter of the copper plate and the coating was connected with the positive terminal.

The data obtained from the decay curve for the active deposit were used for calculating the maximum value for the activity of radium A and radium C by means of the equations given by Rutherford.†

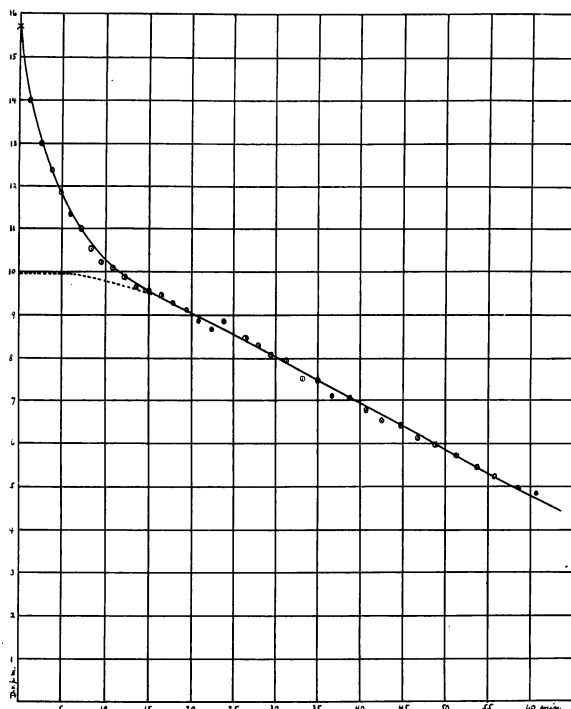
The data furnished by measurements of the most active deposit are shown graphically in figure 3. The ordinates are

* This Journal, xxi, 409, 1906.

† Radio-activity, 2d edition, p. 334. The values taken for the constants were: λ_1 (radium A) = 0.231 (min.) $^{-1}$; λ_2 (radium B) = 0.0266 (min.) $^{-1}$; λ_3 (radium C) = 0.0365 (min.) $^{-1}$. Bronson, Phil. Mag., xi, 73, 1906.

proportional to the activity in divisions per minute and the abscissas are taken as the time in minutes from the instant at which the plate was removed from contact with the emanation. The initial activity for radium C (plus radium B) given by the equations is about 10 div. per min., and for radium A + radium B + radium C about 15.7 div. per minute. The initial activity of radium A was therefore about 5.7 div. per min. An interesting relation is shown by these numbers if considered in con-

3



nection with the ranges in air of the α particles emitted by these products. If it is assumed that the ionization produced by the easily absorbed β radiation from radium B is about 5 per cent of the ionization produced by the α particles from radium C,* the activity of radium C alone is found to be 9.5 div. per min. The ratio of the activities of equilibrium amounts of radium A and C as determined in this manner is

* The results obtained by H. W. Schmidt (*Annal. d. Phys.*, xxi, 609, 1906) and Bronson (*loc. cit.*) afford some basis for this assumption.

the same as the ratio of ranges of the α particles emitted by these substances, namely,

$$5.7 : 9.5 = 4.23 : 7.06.$$

This is an important confirmation of the suggestion made in an earlier paper* that the ionization produced by an α particle is proportional to its range.†

The value found for the activity of radium A and C in the active deposit on the copper plate is only about 60 per cent of the activity to be expected. It is probable that under more favorable conditions the entire equilibrium amount of these products could be obtained.

The results obtained indicate that if the activity of the uranium in a mineral be taken as unity, the activities of radium and its immediate products are approximately the following:

Radium	=	0.45,
Emanation	=	0.62,
Radium A	=	0.54,
Radium B	=	0.04 ?
Radium C	=	0.91,
(Uranium	=	1.00).

Activity of Polonium (Ra F).

About four years ago I carried out some experiments on the separation of the polonium from known amounts of certain uranium minerals. About 10 grams each of uraninite and gummite were taken, the former containing 75 per cent and the latter 63 per cent of uranium. The minerals were dissolved in dilute hydrochloric acid, the solutions evaporated to dryness to remove silica, and the filtrate from the silica, after the addition of a little bismuth nitrate, was treated with an excess of hydrogen sulphide. The sulphides were decomposed with nitric acid, the lead was removed as sulphate, and the bismuth and other substances were precipitated with ammonia.

* Boltwood, this Journal, xxi, 414, 1906.

† Professor Bumstead has pointed out to me that this assumption is in no way contradictory to the evidence furnished by the ionization curves obtained by the Bragg method. A typical Bragg curve for radium C has been given by McClung (Phil. Mag., xi, 135, 1906). On the assumption that the ionization is proportional to the range, the total ionization is considered as proportional to the area of the rectangle measured by the range and the ionization per centimeter for the first centimeter or so of the range. In the Bragg curves the ionization is proportional to the area included within the curve, and the range is taken as the point where the first, upper, well-defined break occurs in the curve. It will be found that the area of that portion of the rectangle which lies without the curve is approximately equal to the area included by the curve which lies without the rectangle. This equality will hold for α particles having a range of 3^{cm} or more; when the range of the α particle is less than about three centimeters the proportionality between range and ionization will be less exact.

After the small precipitate was filtered off and washed, it was dissolved in a small volume of very dilute hydrochloric acid. A button of metallic bismuth was suspended over the solution so that its under side just dipped below the surface of the liquid. The solutions were allowed to stand for about ten days, when the bismuth buttons were removed and their activities compared in an electroscope. The activities found were quite closely proportional to the amounts of uranium in the minerals taken.* The residues obtained when the solutions were evaporated to dryness were found to be almost completely inactive.

Rutherford† has shown that polonium is a direct disintegration product of radium. As a consequence of this it is to be expected that minerals will contain amounts of polonium in proportion to the amounts of uranium and radium present. If the mineral in its natural state loses an appreciable amount of its radium emanation, the amounts of polonium present will be correspondingly reduced.

As the relative activities of the radium and the polonium in a mineral are of some importance, the following experiments were carried out to determine this relation:—

First Series.—Early experiments. In these experiments the polonium was separated from 0.100 gram of uraninite (containing 75.8 per cent of uranium) by the operations already described. Instead, however, of allowing the bismuth buttons to remain in contact with the solutions for a longer period of 10 days or so, the buttons were attached to a short, vertical rod connected with a motor, and were rotated in the solutions for periods of from one to three hours, or longer. The buttons were then removed, washed, dried and their activity determined in the electroscope. The activity of the polonium obtained in this manner was compared with the activity of the uranium present in the mineral taken, with the following results:—

No. 1, $0.33 \times U$; No. 2, $0.37 \times U$; No. 3, $0.44 \times U$.

The periods that the buttons were treated were about one, two and four hours respectively.

Second Series.—Later experiments. The addition of even small amounts of bismuth to the mineral solution previous to the separation of the sulphides introduced certain difficulties later, the most serious of which was the necessity of having considerable free hydrochloric acid present in the final solution in order to prevent the precipitation of the bismuth as a basic salt. When the basic salt was formed it carried with it a large proportion of the polonium. The addition of the bismuth salt was therefore omitted, and an attempt was made to separate

* Eng. and Min. Jour., lxxvii, 756, 1904.

† Phil. Mag., viii, 636, 1904; *ibid.*, x, 290, 1905.

the polonium from a quantity of 1 gram of a uraninite, containing 78.5 per cent of uranium, the process followed being otherwise identical with that already outlined. The precipitate of hydroxides obtained was very small, and was readily dissolved in a couple of drops of dilute hydrochloric acid. This solution was diluted to exactly 50^{cc} and quantities of this, 10^{cc} in volume, were taken for separate treatment with metallic bismuth. In the first experiment the button was rotated in the solution for 3½ hours; in the second the button previously used was run for 4 hours, when a fresh button was put in and run for one hour longer. The polonium on the second button was only about 2.5 per cent of that obtained on the first. In the third experiment, which was made on the day following, a button was run in this solution for 7 hours and a fresh button was then put in and run for one hour longer. The amount of polonium removed on the second button was an inappreciable fraction of that deposited on the first.

The activities of the total polonium obtained in the separate experiments, expressed in terms of the activity of the uranium in the original mineral, were 0.38, 0.34 and 0.22, respectively. It was found, from these and from other experiments, that the polonium was gradually precipitated from very dilute hydrochloric acid solutions on standing, even when the amount of bismuth salts in the solution was inappreciable.

Third Series.—Final experiments. One gram of uraninite (78.5 per cent uranium) was used for these experiments and about 10 milligrams of bismuth nitrate was added to the solution of the mineral in nitric acid before the sulphides were precipitated with hydrogen sulphide. The separation of the polonium was conducted as before. The final hydrochloric acid solution contained 5^{cc} of concentrated HCl and had a volume of 100^{cc}. Portions of this solution 10^{cc} in volume were introduced into a glass cylinder closed at the bottom by a copper plate. The plate was about 2 inches square and was held tightly to the cylinder by clamps; the joint between cylinder and plate was made tight by a washer of thin sheet rubber. The solution in the cell was diluted to about 30^{cc} and was stirred by a small glass stirrer driven by a motor. In the first experiment, conducted with the freshly prepared solution, after a run of 3½ hours, the activity of the copper plate was 4.27 div. per minute. A fresh copper plate treated with the same solution for two hours longer had an activity of 0.10 div. per minute. The total was therefore 4.37 div. per minute per 0.1 gram of mineral, equivalent to 43.7 div. per gram. The amount of uranium in 1 gram of the mineral was 0.785 gram and the activity of the polonium obtained per gram of uranium was therefore $\frac{43.7}{.785} = 55.7$ div. per minute. The activity of

one gram of uranium being 124 div. per minute, the relative activity of the polonium was $\frac{55.7}{124} = 0.45 \times U$.

A second similar experiment made shortly after the first one was completed gave $0.41 \times U$ for the relative activity of the polonium. A third experiment made with 10°C of the same solution after it had stood for 2 days gave the value $0.32 \times U$ for the activity of the polonium, indicating that in this solution also the polonium was slowly separating out in an insoluble form.

The precipitate of lead sulphate removed in preparing the polonium solution was dissolved by warming with some dilute hydrochloric acid to which a few crystals of potassium chlorate had been added,* a little sulphuric acid was then added and the solution was heated until white fumes appeared. The solution obtained by treating the residue of lead sulphate with a drop or two of dilute hydrochloric acid and a little water, was placed in the cell and stirred in contact with a copper plate for about an hour. The activity of the polonium obtained on the plate was equal to 0.80 div. per min. Correcting the activity of the polonium obtained in the first experiment by this amount gives the value of its relative activity as $0.46 \times U$. It would appear that but little of the polonium remains with the lead when the latter is removed as the sulphate.

Attempts were also made to separate the polonium on a platinum plate from a nitric acid solution by electrolysis. The acid solutions tried were of various strengths but the results were very unsatisfactory, the chief difficulty lying in the fact that a greater proportion of the polonium was deposited on the anode than on the cathode. It was also found that in general the chemical separation of the polonium was incomplete when some bismuth salt was not added to the solution of the mineral before the sulphides were precipitated.

The activity of the polonium separated in the three series of experiments varied with the conditions, and the maximum value obtained was $0.46 \times U$. The value to be expected from the theory is somewhat greater than this, namely, about $0.49 \times U$, when the relative ranges of the α particles from radium (3.5^{cm}) and polonium (3.8^{cm}) are taken into consideration and the activity of the radium is assumed to be $0.45 \times U$. That the experimental results should come out somewhat low (about 6 per cent) is not surprising in view of the difficulties attending the separation of so minute an amount of matter.†

* Considerable quantities of lead sulphate can be decomposed by this treatment.

† The weight of polonium in one gram of the uraninite is probably of the order of 5×10^{-11} gram.

That the active substance separated on the copper plates and bismuth buttons was wholly polonium was demonstrated by measurements of its rate of decay, which corresponded closely to that of polonium (Rutherford, *Radioactive Transformations*, p. 127).

Activity of Ionium.

A preliminary notice of the occurrence in uranium minerals of a new radio-active element showing a chemical behavior similar to that of thorium has already been published.* Details concerning the chemical and radio-active properties of this interesting substance will be given in a later paper,† where it will be shown that ionium emits α particles having a range of approximately 2.8^{cm} in air and is the immediate substance from which radium is produced. For the present it will be assumed merely that the ionium is separated with the thorium in a mineral, an assumption which is supported by the experiments of Hahn,‡ who has observed its presence in the purified thorium salts prepared by technical methods.

Experiment 1. One gram of uraninite (No. 4, Table IV) was decomposed by heating with dilute nitric acid and the solution was evaporated to dryness. The residue was treated with a few drops of nitric acid and hot water, and the insoluble matter was filtered off. The sulphides were precipitated with hydrogen sulphide and removed. After the removal of the excess of hydrogen sulphide exactly 0.2 gram of thorium nitrate was added to the solution. This nitrate had been prepared shortly before by a method which insured its freedom from mesothorium,§ and the proportion of thorium oxide in the salt had been accurately determined. The solution was heated to boiling, an excess of oxalic acid was added, and the mixture was allowed to stand for 24 hours. The precipitated oxalates were filtered off, and ignited. The oxides were fused with sodium bisulphate and the melt dissolved in water. The precipitation with oxalic acid was repeated, the oxalates were converted into oxides by intense ignition over the blast-lamp, and the weight of the oxides was accurately determined. A portion (90 per cent) of the oxides was removed, again converted into the soluble sulphate, and the rare earths were precipitated as hydroxides with ammonia. The hydroxides, after thorough washing with hot water, were dissolved in hydrochloric acid and the solution was evaporated to dryness. A few drops of dilute hydrochloric acid were added to the residue of

* Boltwood, this Journal, xxiv, 370, 1907; *Nature*, lxxvi, pp. 544, 589, 1907.

† This Journal, May, 1908.

‡ *Ber. d. chem. Ges.*, xxx, 3304, 1907; *ibid.*, xxx, 4415, 1907.

§ Boltwood, this Journal, xxiv, 93, 1907.

chlorides, which was then treated with water. The solution was filtered to remove traces of silica. The filtrate, diluted to a volume of about 100^{cc}, was heated to boiling, an excess of sodium thiosulphate was added, and the mixture was boiled until the free sulphurous acid was completely removed. The precipitate, containing free sulphur, was filtered off and treated with dilute hydrochloric acid. The solution was filtered and the precipitation with sodium thiosulphate was repeated. The second precipitate was ignited at a high heat in a platinum crucible over the blast-lamp. The thorium oxide obtained in this manner weighed 0.0878 gram. A film containing 0.0123 gram of this oxide was prepared.

The activity of the film when first prepared was 4.53 div. per minute. The activity rose for about 30 days and then fell very slowly.* At the end of 110 days the activity of the film was 4.75 div. per minute. This was equal to 37.7 div. per min. per gram of the mineral taken. The correction for the activity of the thorium and thorium products present was now calculated and was found to be equal to 5.7 div. per min. for the total activity.† The activity of the ionium from the mineral was therefore equal to 32.0 div. per minute. Dividing this by the activity of the uranium in one gram of mineral (0.758×124) gives the value $0.34 \times U$ for the relative activity of the ionium.

Experiment 2. One gram of Branchville uraninite (No. 2, Table IV) was taken for this experiment. The material was treated in the same manner as was the North Carolina uraninite in Experiment 1 and the film of thorium oxide finally prepared showed the same proportionate variations in its activity. The activity of the film at the end of 110 days was equal to 3.88 div. per min. This corresponded to 41.7 div. per min. for the activity of the total oxide and the correction for the thorium products present was 10.6 div. per min. The activity of the ionium from one gram of the mineral was therefore 31.1 div. per minute. When this is divided by the activity of the uranium (0.777×124), the value 0.32 is found for the ratio of the activity of the ionium to that of the uranium with which it is associated.

Experiment 3. In this experiment one gram of North Carolina uraninite (No. 3, Table IV) was taken. After the

* The initial rise was due to the formation of thorium X and its products, which had been removed by the chemical treatment. The subsequent fall was due to the decay of the radiothorium present.

† To determine this correction a film of thorium oxide was prepared from the nitrate added to the mineral solution. This film was measured in the electroscope at the end of the 110 day period. The activity of the thorium in the mineral was calculated directly from the rates of decay of radiothorium and mesothorium.

removal of the insoluble matter and the sulphides precipitated by hydrogen sulphide, the solution was evaporated to dryness. The residue of nitrates was heated for some time at 110° to remove all excess moisture and was then extracted with ether. The oxalates precipitated from a dilute nitric acid solution of the residue remaining after treatment with ether (as described under the heading "Determination of Uranium," page 276), were converted into the oxides and dissolved as sulphates after fusion with sodium bisulphate. From the solution obtained, the rare earths were precipitated as hydroxides by ammonia and the thorium was separated by treatment with sodium thiosulphate, twice repeated. The final precipitate was dissolved in dilute hydrochloric acid, the sulphur present was filtered off, and the thorium was precipitated as hydroxide by ammonia. The thorium hydroxide was finally ignited strongly to form the oxide, and from this oxide a film weighing 0.00735 gram was prepared. The activity of this film was 13.0 div. per min. at the start; it rose slightly at first and then fell slowly like the others; and at the end of 128 days amounted to 12.8 div. per minute. This was equivalent to 33.3 div. per gram of mineral and the amount to be deducted for the thorium present was 2.2 div. The activity of the ionium was therefore 31.1 div. per minute and its relative activity was 0.32 as compared with the activity of the uranium present.

Experiment 4. One gram of the same mineral used in Experiment 3 was taken and the chemical treatment to which it was submitted was identical, except that the thorium was not separated from the other rare earths by precipitation with sodium thiosulphate. Instead, the combined hydroxides precipitated by ammonia were directly ignited to form the oxides and a film was prepared from this material. The activity of this film rose steadily from the start, and at the end of 129 days had increased by 64 per cent of its initial value. It will be shown later that the rise was due to the presence of actinium in the oxides and that the activity due to the actinium in the freshly prepared oxide was practically equal to zero. The initial activity of the film, corrected for the thorium products present (radiothorium only), was therefore due only to ionium and was equivalent to an activity of 34.3 div. per minute for the ionium in the mineral taken. This gives a value of $0.35 \times U$ for the relative activity of the ionium in the mineral.

The values for the relative activity of the ionium obtained in these four experiments were therefore 0.34, 0.32, 0.32 and $0.35 \times U$.

Activity of Actinium.

The most difficult problem encountered in the course of this investigation was the separation of the actinium from the min-

erals. The difficulty was due chiefly to the fact that most of the chemical properties attributed to this element by Debierne* are not possessed by it, but are characteristic for two quite different substances, namely, thorium and ionium.

The fact that actinium is precipitated with the rare earths was noted by Giesel,† and its further property of not being precipitated with thorium by sodium thiosulphate has been observed by Marckwald‡ and by Giesel.§ In the experiments which will next be described advantage was taken of these properties, and the actinium was precipitated from the solutions of the rare earths after the removal of the thorium.

Experiment 1. The filtrates obtained after removing the thorium and ionium precipitated by sodium thiosulphate as described under "Activity of Ionium," "Experiment 3," were combined and concentrated by evaporation. An excess of hydrochloric acid was added and, after boiling to decompose the sodium thiosulphate present, the separated sulphur was removed by filtration. The solution was still further concentrated, and finally in a volume of about 50^{cc} the rare earths were precipitated as hydroxides by ammonia. The hydroxides were filtered off and intensely ignited to form the oxides. From the oxides, having a total weight of 0.0068 g., a film weighing 0.0037 g. was prepared. The activity of the film when freshly prepared was less than 0.10 div. per min. The activity rose slowly and at the end of 128 days reached a value of 7.55 div. per min. This corresponded to 13.9 div. per minute for the total oxide. Dividing this by the activity of the uranium in the gram of mineral taken gives $0.14 \times U$ for the relative activity of the actinium separated. That the active substance was certainly actinium was demonstrated by the rate of rise of the activity, which is shown in figure 4. In this diagram the ordinates represent the activity and the abscissas the time in days. The maximum activity is taken as 100. The crosses give the activities as measured and the curve is the recovery curve for actinium from which all active products have been removed.|| The slight irregularity at the start was probably due to the presence of small amounts of products in the fresh oxide.

Experiment 2. In this experiment the filtrates obtained in Exp. 1, "Ionium," were treated as described in Experiment 1 of this series (Actinium). The ignited oxides of the rare earths were made into a film weighing 0.0065 gram. The activity of the film at the start was 0.45 div. per min., and the activity

* C. R., cxxix, 593, 1899; *ibid.* cxxx, 206, 1900.

† Ber. d. chem. Ges., xxxv, 3608, 1902.

‡ Ber. d. chem. Ges., xxxviii, 2264, 1905.

§ Ber. d. chem. Ges., xl, 3011, 1907.

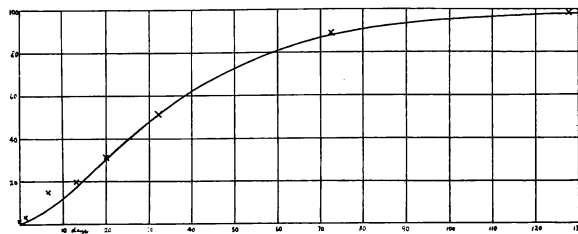
|| Hahn, Phil. Mag., xiii, 165, 1907.

rose at a rate corresponding to the growth of products in actinium. At the end of 110 days the activity of the film was 4.05 div. per minute, which corresponded to 14.1 div. per minute for the equilibrium value of the actinium separated with the total oxides. The relative activity of the actinium products obtained in this case was therefore $0.15 \times U$.

Experiment 3. The amount of actinium in the mineral was calculated from the rise in the activity of the film described under "Experiment 4, Ionium." The activity of this film at the end of 129 days was corrected for the activity of the thorium products present. The initial activity (corrected for thorium products) had been equivalent to $0.34 \times U$; the final activity (similarly corrected) was equal to $0.58 \times U$. The difference, amounting to $0.24 \times U$, could be attributed to the actinium (and products) in the mineral.

Experiment 4. A portion of the oxides of the rare earths separated as oxalates in "Experiment 1, Ionium," was made into a film about six months later. Another small portion of

4



the oxides was tested by the emanation method and found to be free from appreciable quantities of radium. The activity of the film corresponded to an activity of $0.71 \times U$ for the total material separated, after a correction had been made for the activity of the thorium products. It is regretted that the activity of this film was not followed from the time when it was first prepared, although a strict interpretation of any variations which might have been noticed would have been difficult owing to uncertainty as to the products contained in it. Assuming that the final activity was due to actinium and ionium only, and deducting the maximum value of $0.35 \times U$ found previously for the ionium, gives a maximum value of $0.36 \times U$ for the relative activity of the actinium products in a mineral.

I am inclined for various reasons to believe that this is more nearly the correct value. It has been observed by both Hahn* and Levin† that the precipitation of actinium by ammonia is

* Phil. Mag., xiii, 165, 1907.

† Phys. Zeit., viii, 129, 1907.

very uncertain and often incomplete. In the course of some further experiments, which will be described in a later paper, where larger quantities of minerals were used, the data obtained on the chemical behavior of actinium indicated that the quantitative separation of this radio-element and its subsequent complete recovery are matters of considerable difficulty. The investigations of other experimenters have been directed chiefly toward determining its qualitative characteristics, so that the information to be found in the literature is of but little assistance.

Other Experiments.

Activity of Heated Minerals.—That a greater or less proportion of the radium emanation contained in minerals can be expelled by heating has been observed by Strutt.* About one gram of the uraninite No. 4 (Table IV) in the form of fine powder was placed in a porcelain crucible, which was enclosed in a covered platinum crucible and heated to bright redness for about ten minutes over a Bunsen burner. The loss in weight of the mineral was determined (3.21 per cent) and a film was prepared from the heated material. About three hours after heating, the activity of this film was measured and at the same time the proportion of the total amount of radium emanation present was determined in a duplicate sample of the ignited mineral. It was found that the ignited mineral contained 46 per cent of its equilibrium amount of radium emanation. After correcting for the activity of the thorium products present, the activity of the uranium and its products† in the film was found to be equal to 3.51 times the activity of the uranium only.

A few days later (3 days 19 hours after the first measurement) the activity of the mineral in the film was again measured, and the activity of the uranium and its products was found to have risen to $4.08 \times U$. When a further period of 26 days from the start had elapsed the corresponding activity was $4.75 \times U$. Four months later the activity was $4.72 \times U$, and the same value was found when the film was measured about 17 months from the time of heating. It was found that after it had been heated, the mineral retained over 99 per cent of the total radium emanation subsequently formed.

It is apparent that the final activity reached by the ignited mineral was the same as that found for a natural mineral containing equilibrium amounts of all the products. This indicates that the amount of polonium expelled by the heating was inappreciable and allows the activity ($3.51 \times U$) found for the freshly ignited material to be taken as a measure of the activity

* Proc. Roy. Soc., lxxiii, 191, 1904.

† By "uranium and its products" is meant the uranium and all other active substances except thorium products contained in the mineral.

of uranium and its products *less* 54 per cent of the equilibrium amount of radium emanation, radium A, radium B and radium C. The difference between the initial and final activities, namely, 4.72 less 3.51 , equals $1.21 \times U$; and this value can be considered as equivalent to 54 per cent of emanation and products. This corresponds to a value of $2.24 \times U$ for the relative activity of the total amounts of radium emanation, A, B and C, a number which is in good agreement with the value $2.09 \times U$ found by the more direct method (p. 283).

The indications that none of the polonium was volatilized in heating the mineral as described were somewhat unexpected, as this active product is quite readily driven off by similarly heating more concentrated preparations. A further quantity of the mineral was therefore heated in a porcelain crucible over the blast-lamp. The activity of the ignited material was only about 2.0 times the activity of the uranium present. After about thirty days the activity of the uranium and the uranium products was equal to about $3.8 \times U$, and this value increased during a further period of about 12 months to $3.95 \times U$. It is probable, therefore, that at the higher temperature a large part of the polonium as well as portions of the other more permanent products were removed. In the case of another portion of the mineral heated to an equally high temperature in an atmosphere of pure oxygen the activity of uranium and its products was reduced to $3.17 \times U$ and the corresponding value four months later was $4.41 \times U$.

It was noted in general that the emanating power of a mineral was greatly reduced by heating. A sample of carnotite which lost 12 per cent of its radium emanation in the natural state lost only 1.4 per cent after it had been heated to a very low red heat.

Activity of Old Radium.—Rutherford has shown that polonium is a disintegration product of radium. As he has pointed out,* it is to be expected that old preparations of radium will contain appreciable amounts of polonium, the actual amount depending on the age of the radium salt and the rates of disintegration of the products. The standard solution of radium bromide prepared by Rutherford, Eve and Boltwood† was made from pure radium which is now at least four years old. A portion (10^{cc}) of this solution containing 1.57×10^{-8} gram of radium was recently evaporated to dryness in a shallow platinum tray and the activity of the radium free from emanation and immediate products was determined in the electroscope. The activity of the uranium with which 1.57×10^{-8} gram of radium would be in radio-active equilibrium was then calculated. It was found that the activity of

* Phil. Mag., x, 290, 1905.

† This Journal, xxii, pp. 1 to 7, 1906.

the radium deposit from the standard solution was approximately 0.52 of the activity of the uranium with which it would be associated in a mineral. This is about $0.07 \times U$ higher than the value obtained with a freshly prepared radium salt (p. 282). If the amount of polonium to be expected in the old radium salt is calculated from the half-value period (12 years) of radium D as recently determined by Meyer and Schweidler* and the half-value period of radium F (polonium) generally accepted (143 days), it is found that about 17 per cent of the equilibrium amount of polonium would be formed in a period of four years. The relative activity of seventeen per cent of polonium would be 0.48×0.17 , namely, $0.08 \times U$, and this number is in good agreement with the value found above.

Emanating Power of Radium Sulphate.—It was noted in the course of certain experiments that the emanating power of radium sulphate in the form of a thin film was not a negligibly small quantity. From a film containing about 10^{-9} gram of pure radium sulphate per square centimeter the loss of radium emanation was nearly 10 per cent of the total. The radium salt had been dried by heating to a low red heat.

Relative Amounts of Radium and Uranium in Minerals.

The value for the amount of radium in equilibrium with one gram of uranium in a mineral given in the paper by Rutherford and Boltwood† is somewhat in error because of the incorrect assumption as to the proportion of uranium in the mineral used.‡ Instead of 68.2 per cent of uranium the mineral actually contained 75.8 per cent of uranium. The amount of radium associated with one gram of uranium in a mineral is therefore about 3.4×10^{-7} gram, instead of 3.8×10^{-7} gram.

Relative Activity of Radium and Uranium.

The relative activity of the radium present in a uranium mineral has been shown to be 0.45 times the activity of the uranium with which it is associated. The amount of radium associated with one gram of uranium in the same mineral has been found to be 3.4×10^{-7} gram. One gram of uranium will therefore have the same activity as 7.5×10^{-7} gram of radium, and one gram of radium (free from all products) will have the same activity as 1,300,000 grams of uranium. One gram of radium containing its equilibrium amount of the products radium emanation, radium A, radium B, and radium C will have about the same activity as 7.3×10^6 grams of

*Phys. Zeit., viii, 457, 1907.

†This Journal, xxii, 1, 1906.

‡The error arose from the difficulty encountered in obtaining a pure uranoso-uranic oxide. Page 282.

uranium. The activity of one gram of pure, anhydrous radium bromide (58 per cent Ra) over 30 days old and retaining all of its emanation will therefore be the same as that of about 4,200,000 grams of pure uranium. These values are based on the assumption that the radium bromide used by Rutherford and Barnes,* for determining the heating effect of radium, was pure, since this material was used in the preparation of the standard solution.

Dealers and manufacturers of radium bromide are in the habit of using as a measure of the activity of the pure salt the expression " $1,800,000 \times \text{Uranium}$." I have never found a definite statement as to the exact meaning of this expression or the manner in which the activity is determined. I have observed,† however, that thin films obtained by the evaporation of dilute solutions of radium bromide may retain less than fifty per cent of the emanation formed within them, so that the number " $1,800,000 \times \text{Uranium}$ " may express with a rough degree of approximation the activity of pure radium bromide measured under similar conditions.

Summary of Results.

The values for the relative activities of the uranium and the various products contained in a uranium mineral which are indicated in the preceding experiments can be expressed as follows, the activity of the uranium being taken as unity :

Element	Activity
Uranium	1.00
Ionium	0.34
Radium	0.45
Radium emanation	0.62
Radium A	0.54
Radium B	0.04 (?)
Radium C	0.91
Radium F (polonium)	0.46
Actinium products	0.28

Total activity $4.64 \times \text{Uranium}$.

If the value to be theoretically expected for the relative activity, namely, $0.49 \times U$, be taken for radium F, and also the maximum values found for the activity of ionium ($0.35 \times U$) and the actinium products ($0.36 \times U$), the sum of the separate activities is equal to $4.76 \times U$. These numbers are in good agreement with the corresponding value of $4.69 \times U$ found from the direct measurement of the uranium minerals. The numerical value of these different quantities will show more or

* Phil. Mag., viii, 202, 1904.

† This Journal, xxi, 414, 1906.

less marked variations when the relative activities are measured in an ionization chamber of different size and dimensions from that of the electroscope used in these experiments. In a smaller ionization chamber the relative activity of the products emitting α particles of longer ranges will be less, while in a larger chamber the ionizing effects due to the various β radiations will be proportionately greater. Without special definition, therefore, the numbers as derived above can not be considered as approximating to definite constants.

The values found indicate that the activity of the uranium is about 2.22 times that of the radium with which it is in radio-active equilibrium. It seems very certain that the range of the α particles from uranium is not greater than the range of the α particles from radium itself,* and the number found is, therefore, not the one which would be expected on the basis of the simple disintegration theory, in which it is assumed that the same number of α particles is emitted per second by equilibrium amounts of successive products. It is possible, however, that two distinct α ray changes may exist in ordinary uranium, although the assumption of two such products does not entirely obviate the difficulty. The problem is evidently too complicated to permit of any simple explanation of the relations for the present.

In so far as these experiments throw any light on the question of a genetic relation between actinium and uranium, I think that the constancy of the activity of the different minerals and the fact that quite appreciable amounts of actinium can be separated from all of them† make it necessary to assume that the amounts of actinium in a mineral are proportional to the quantity of uranium present. It is therefore extremely probable that actinium is a disintegration product of uranium, although its position in the uranium-radium series is still to be determined.

New Haven, Conn.,
February 14, 1908.

* Bragg, *Phil. Mag.*, xi, 754, 1906. McCoy and Ross, *Jour. Am. Chem. Soc.*, xxix, 1698, 1907.

† I have had no difficulty in demonstrating the presence of actinium in carnotite.