[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Beta-Ray of Actinium

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Introduction

Although actinium was discovered early in the history of radioactivity[1] and has since been the subject of much experimental study, all previous attempts to find any effect due to the radiation from actinium itself have met with failure. In the purest samples of actinium investigated,[2] which were studied by means of ionization chambers, only very feeble effects were noted, which could not be distinguished from the effects of very slight impurities. The fact that the direct descendant of actinium is radioactinium,[2a] an isotope of thorium, indicates that a beta-particle must be emitted in the disintegration of actinium. Because this beta-particle has not been observed experimentally, it has been customary to assume that it is emitted with a very low energy. The discovery by Sargent[3] of the relation between the decay constants of beta-emitters and the upper limits of their energy spectra lent added interest to the energy of the actinium beta-particle, which apparently was anomalous.

With the modification of the tube counter devised by Libby,[4] in which a screen wall is substituted for the customary solid wall, it is possible to detect electrons of very low energy, probably as low as a few volts. Hence it seemed likely that with this instrument it should be possible to obtain experimental evidence for the actinium beta-ray, and possibly to measure its energy. This paper presents the results of such an investigation.

Apparatus

The counter used for most of the experiments described below was 11.5 cm. long and 1.6 cm. in diameter. The wall was of copper screen, made of No. 31 (0.009 in.) wire, 35 to the inch; the average open space for soft radiations was 40%. The wire of the counter was No. 30 iron wire. This counter, when filled with argon at a pressure of 12 mm. operated at around 700 volts. The voltage was supplied by rectifiers from a 500-cycle motor-generator set, through a Street–Johnson voltage regulator. A vacuum tube resistor was connected between the counter wire and the ground. The impulses were amplified and recorded automatically through a scale-of-four thyratron circuit. The counter was mounted inside an air-tight chamber. The samples to be tested were mounted on the inside of one-half of a brass cylinder arranged coaxially with the counter. The cylinder was tilted back and forth to expose or remove the sample at will.

Extraction and Purification of Actinium

The actinium used in these experiments was extracted from a sample of the residue of a Colorado uranium ore from which the radium had been removed. The final product was a yellow solid consisting largely of cerium and other rare earths.

An analysis of the radioactive substances present in the sample was made by the following method. A few grams of the rare earth chlorides was dissolved in dilute hydrochloric acid, and a little lead salt added. This was precipitated as lead sulfide by bubbling hydrogen sulfide through the hot solution. The precipitate was filtered and washed, and sealed into a test-tube as rapidly as possible. The tube was then fixed in a position adjacent to the counter, and the gamma-ray activity watched over a period of several hours. An initial count of 270 per minute decayed exponentially with a half-life of thirty-seven minutes, to a residual activity of 11 per minute over the background (28 per minute). Since actinium B, which is the radioactive isotope of lead in the decay series of actinium, has a known half-life of thirty-six minutes, this result shows conclusively that the chief radioactive constituent of the sample is actinium. The other possible constituents of the sample, radium and thorium, would have been accompanied by radium B and thorium B, respectively, with half-lives of 26.8 minutes and 10.6 hours. The presence of the first of these substances in appreciable amount in the lead sulfide precipitate would have led to an initially steeper portion of the decay curve, while the second would have caused a tail with a slower decay. Certainly less than 5% of the activity was due to either of these elements. The final activity could not have been due to thorium B, because it persisted after two days. It was presumably due to a little actinium retained by the filter paper.

The next step was to purify the actinium from radioactinium, actinium X and actinium B, isotopes, respectively, of thorium, radium and lead. The other decomposition products of actinium are so short-lived as to make their removal unnecessary. The actinium B is removed by adding a little lead chloride and precipitating with hydrogen sulfide in 0.2 *N* acid. The usual method for the removal of radium, through the precipitation of barium sulfate from the solution, is not applicable in this case, because actinium is strongly adsorbed on barium sulfate. The older method of precipitating the actinium with hydroxides by ammonia, leaving the radium in solution, is not entirely trustworthy because the complete precipitation of actinium is uncertain in the presence of ammonium ion. Furthermore, since the adsorption phenomenon

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(1) Debierne, *Compt. rend.*, **129**, 593 (1899); **130**, 906 (1900); **131**, 333 (1900); **139**, 538 (1904). Giesel, *Ber.*, **35**, 3608 (1902); **36**, 342 (1903); **37**, 1696, 3963 (1904); **38**, 775 (1905).

(2) (a) Hahn and Rothenbach, *Phys. Z.*, **14**, 409 (1913); (b) Meyer, Hess and Paneth, *Sitzb. Akad. Wiss. Wien.*, **123**, 1459 (1914).

(3) Sargent, *Proc. Roy. Soc.* (London), **A139**, 659 (1933).

(4) Libby, *Phys. Rev.*, **46**, 196 (1934).

tends to contaminate the precipitate with the ions in solution, it is preferable to have the undesirable impurity in the precipitate in every separation. Therefore, it was attempted to make use of the precipitation of barium chromate in a solution buffered with acetic acid and acetate ion. The fact that the rare earth chromates as well as calcium chromate are soluble, indicated that actinium might not be precipitated in this process. Tests proved that the separation was satisfactory if the solution was carefully buffered. Two equal samples were treated identically in every way in their purification, except that in the precipitation of barium chromate, one was carried out with the hydrogen-ion concentration 2×10^{-6}, and the other 2×10^{-4}. The final sample in the first case was completely inactive, while the second was quite active. This result indicated that actinium is precipitated with barium in the less acid solution.

The removal of radioactinium proved the most troublesome. Experiments were tried based on the coprecipitation with zirconium by iodate and thiosulfate, but the results were not satisfactory. Finally the coprecipitation with thorium peroxyhydroxide was adopted. The thorium used was carefuly purified from mesothorium 1 and 2, the latter being isotopic with actinium.

The final procedure was as follows. The sample was dissolved with a trace of the purified thorium chloride and of barium nitrate in 30 cc. of 6 N acetic acid to which was added 3 cc. of saturated (5–6 N) sodium acetate. The solution was heated to boiling, and an equal volume of 2 N sodium dichromate was added. After standing for ten minutes the barium chromate was filtered out. The filtrate was made alkaline with sodium hydroxide and sodium carbonate. The rare earth and thorium carbonates were filtered and washed (to remove chromate and acetate, which would char in the subsequent evaporations) and redissolved in hydrochloric acid. A little lead chloride was added to the solution, and it was evaporated to dryness. This residue was dissolved in 30 cc. of water with 1 cc. of 6 N hydrochloric acid, heated to boiling, and hydrogen sulfide passed in. The lead sulfide was filtered out and the filtrate was evaporated until no odor of hydrochloric acid could be detected. The residue was dissolved in 2 cc. of water with one drop of 6 N hydrochloric acid, 5 cc. of 1 M hydrogen peroxide was added, and the test-tube was heated in a beaker of almost boiling water for ten minutes. Then the thorium peroxyhydroxide was filtered, and the filtrate was evaporated, thus obtaining the rare earth chlorides with radioactively pure actinium.

Experiments with Purified Actinium

In the first experiments made with the purified actinium, the sample was mounted on one-half of a sample cylinder in the usual way. A large effect, as much as several hundred per minute, was noted immediately, thus yielding the first evidence that the actinium radiation was experimentally detectable. Evidence that this effect was really due to actinium, and not to its decay products present through the failure of the chemical separations, was found through the use of an aluminum shield, 0.0023 g./sq. cm. in thickness. The effect of the purified sample was first measured without the shield, then the whole of the inside of the cylinder was covered with the foil, and the effect again measured. The results of four different experiments are given in Table I. The thickness of the sample was about 0.0001 g./sq. cm.

TABLE I

EFFECT OF 0.0023 G./SQ. CM. SHIELD ON ACTINIUM RADIATION

Effect (counts per minute) Without shield	With shield	Fraction penetrating, %
18.5 ± 0.9	7.3 ± 1.2	39 ± 6
12.9 ± 1.2	5.0 ± 0.9	39 ± 8
29 ± 1.2	15 ± 1.0	52 ± 4
55 ± 2.0	29 ± 2.0	53 ± 4
	Weighted average	48 ± 3

This strong absorption of the radiation in such a thin foil pointed to a weak beta-particle. The slowest alpha-particle in the actinium decay series has a range twice as great, and the beta-particles from actinium B and actinium C″ have ranges of a much greater magnitude. None of the radiations from the decay products could be affected by this foil to the extent observed. A better estimate of the energy of the disintegration electrons was made on the basis of results obtained by using the counter with the sample in a magnetic field. These experiments were carried out with equipment similar to that described by Libby[4] and used by him in the study of the neodymium beta-particle. A magnetic field applied in the direction of the axis of the counter was varied in strength and the effect at each field strength was measured. The results are shown in Fig. 1. Because of the difficulty of shifting the sample back and forth inside the magnet, the background was not measured along with the exposed rate, but the average of the three points with the strongest fields is about the right background for the counter used. At a field of 2060 gausses the effect of the sample disappeared. Taking into account the dimensions of the counter and sample cylinder (1.4 and 3.1 cm. in diameter, respectively), this corresponds to a maximum $H\rho$ of 1750 gausses-cm., which is taken as the upper limit of the energy of the actinium electron. The fact that the radiation can be deflected in this way is experimental proof that it consists of electrons. Electrons of $H\rho$ 1750 have a maximum range of 0.05 g./sq. cm. The half-value thickness of 0.0023 g./sq. cm. is consistent with this upper limit. $H\rho$ 1750 corresponds to an energy of about 220,000 electron-volts. Plotting this figure against the decay constant of actinium on the Sargent diagram,[3] it is found that actinium falls on the lower curve.

At this point, a summary of the evidence at hand pointed unmistakably to a new radiation, which was very probably to be ascribed to actinium. However, to obtain convincing proof that the radiation does come from actinium, and not from any possible remaining impurity, it was desired to see how the activity changed with time.

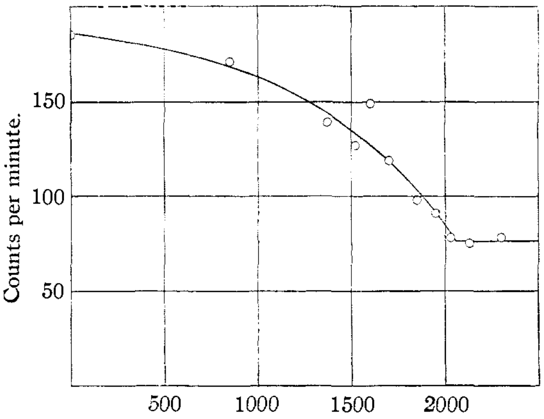

Fig. 1.—Actinium radiation in magnetic field.

The life of actinium being longer than that of any of its decay products, the latter slowly grow in a sample of initially pure actinium, until they come into equilibrium with it. The change of activity due to this growth has been calculated and is shown by the light lines in Fig. 2. The growth curve of a radioactive substance is a characteristic which distinguishes it uniquely from all other substances, since it depends upon the periods of the various decay products, and these periods vary over such a tremendous range of values that no two different radioactive substances have growth curves at all similar, when plotted on the same time scale.

The growth curve of the actinium was measured in this way. A sample was freshly purified and mounted in the usual way on one half of a cylinder. Its activity was measured as soon as possible after its purification. Then the whole cylinder was covered with the aluminum foil, partly to reduce the total effect by shielding out half of the beta-particles, but chiefly to prevent the escape of actinon, which would distribute a large fraction of the activity around the chamber, and inside of the counter. With this arrangement the activity was measured from day to day over a period of three weeks. The results are plotted in Fig. 2. The calculated curve was obtained by drawing the best straight line through the data between ten and twenty days, as the theoretical curve shows that in this interval the increment should be linear, and then drawing in the rest of the curve to fit the alpha plus strong beta curve. The total increment in the activity at the end of eleven and one-half days should equal the initial beta activity of the actinium. By a coincidence, the initial activity came out just 50 per minute, which was the figure taken beforehand in drawing the calculated curves. The broken line has been drawn in to show the total activity, if no shield were used and if no actinon escaped. This is not experimentally realizable, except at the beginning, when the amount of actinon is quite small. The single measurement made in this way agrees well with the calculated curve. The heavy solid line shows the activity to be expected with the shield covering the sample. Only one or two of the points on the whole curve are outside the observational error inherent in counting random events.

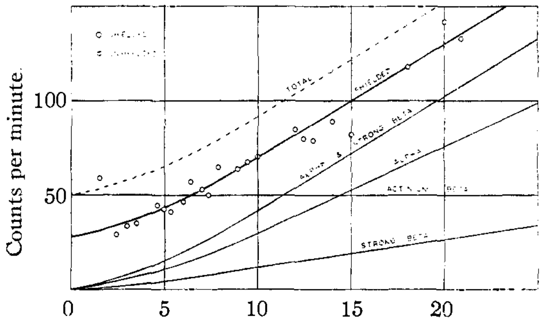

Fig. 2.—Growth of actinium activity.

The excellent agreement of the experimental points with the theoretical curve proves beyond any reasonable doubt that the observed activity is due to actinium.

Summary

The detection of the beta-particle of actinium has been accomplished through the use of the screen-wall tube counter. The actinium, in a body of rare earth chlorides, was carefully purified by co-precipitation methods and mounted in a very thin layer on a cylinder around the counter. Effects of several hundred counts per minute were easily obtainable. The radiation is half absorbed in 0.0023 g./sq. cm. of aluminum. It is easily deflected away from the counter when it is placed in a magnetic field. The maximum energy of the beta-particles is about 220,000 electron-volts, which value fits well on the lower Sargent curve.

The radiation has been positively identified as due to actinium itself by the excellent agreement between theoretical and experimental growth curves.

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The Kinetics of Hypobromite Decomposition

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This study has been undertaken to determine the order of decomposition of hypobromites in weakly acid and weakly alkaline solutions, as well as the effect of *p*H on the reaction velocity.

Earlier investigations show that bromate formation in strongly alkaline solutions is second order with respect to concentration of hypobromite; as the alkalinity of the solution is decreased, a third order reaction appears and may become predominant under the proper experimental conditions. Liebhafsky and Makower[1] from a consideration of their own work, that of Skrabal and Weberitsch[2] and that of Kretzschmar[3] infer that the rate of decomposition of hypobromite can be represented by the equation

$$-\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = k_{c''}\,[\mathrm{HBrO}]^2\,[\mathrm{BrO^-}] \qquad (1)$$

Corresponding to the rate determining step

$$2\mathrm{HBrO} + \mathrm{BrO^-} = \mathrm{BrO_3^-} + 2\mathrm{H^+} + 2\mathrm{Br^-}$$

as originally suggested by Kretzschmar. Equation (1) can be translated into an alternate form by introducing the ionization constant, K_{HBrO}, of hypobromous acid and the ion product of water, K_w, namely

$$-\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = k_3\,[\mathrm{HBrO}]^3\,[\mathrm{OH^-}] \qquad (2)$$

where $k_3 = k_{c''}\,K_{\mathrm{HBrO}}/K_w$. According to this equation the reaction is of the third order with respect to hypobromous acid at constant *p*H and varies with the latter as the first power of the $\mathrm{OH^-}$ concentration.

In a more recent paper Chapin[4] finds the reaction in line with the above to be of third order in strongly acid solutions and of second order in solutions of *p*H 9 or higher. The hydrogen-ion concentration was determined by Chapin colorimetrically after first destroying the oxidizing agents in solution.

In this work the rate was followed at 25° in solutions of various constant hydrogen-ion concentrations in the range *p*H 6.4 to 7.8. Constant *p*H was maintained with $\mathrm{Na_2HPO_4}$–$\mathrm{NaH_2PO_4}$ buffers, while the hydrogen-ion concentration was determined with a glass electrode and vacuum tube voltmeter.

Experimental

Apparatus

Constant Temperature Bath.—The water bath used was of large capacity and was maintained at 25 ± 0.05°.

Glass Electrode.—The electrode used was of the type described by Robertson[5] and others, and was made of Corning 015 glass. Before and after every experiment the electrode was calibrated by two buffers whose *p*H fell on either side of that of the solution studied. A straight line relationship was assumed between these voltages and *p*H, an assumption amply borne out by calibration of the electrode over the *p*H range 2 to 8.5.

Vacuum Tube Voltmeter.—The vacuum tube voltmeter was of the usual type. Plate current deflections were compensated by an external e. m. f. whose value was measured with a Leeds and Northrup student type potentiometer.

Reaction Vessel.—The reaction vessel consisted of a three-necked liter flask.

Analytical

At intervals samples were removed from the reaction vessel and analyzed for hypobromite content and total oxidizing power. The hypobromite concentration was determined by adding a definite volume of solution to an excess of standard arsenite solution and titrating the excess with iodine. Toward the end of the titration excess bicarbonate and starch were added and the titration continued to the well-known blue end-point.

The total oxidizing power was determined by adding definite volumes of sample to solutions of potassium iodide acidified with hydrochloric acid, and titrating the liberated iodine with thiosulfate, using starch as an indicator. The difference between total oxidizing power and total hypobromite represents the concentration of bromate.

Procedure

In this study the hypobromite solutions were kept at constant *p*H during the course of an experiment with mixtures of $\mathrm{Na_2HPO_4}$ and $\mathrm{NaH_2PO_4}$ as buffers. (In two cases mixtures of $\mathrm{KH_2PO_4}$–$\mathrm{K_2HPO_4}$ were used.) The former was about 0.13 molar, while the latter was 0.5 molar. By mixing the two in various proportions with the hypobromite solution, the *p*H range of 6.4 to 7.8 could be easily covered.

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(1) Liebhafsky and Makower, *J. Phys. Chem.*, **37**, 1037 (1933).

(2) Skrabal and Weberitsch, *Monats.*, **36**, 237 (1915).

(3) Kretzschmar, *Z. Elektrochem.*, **10**, 789 (1904).

(4) Chapin, THIS JOURNAL, **56**, 2211 (1934).

(5) Robertson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 5 (1931).