THE RELATION BETWEEN ALPHA-RAY ACTIVITIES AND RANGES IN THE ACTINIUM SERIES, WITH NOTES ON THE PERIOD AND RANGE OF RADIOACTINIUM

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IT now seems well established that the number of ions, and therefore the ionization current in air due to a single particle of range R is very closely proportional to $R^{\frac{2}{3}}$.[1] In a recent paper,[2] it has been shown that the activity of each α-ray product of the thorium series is proportional to the 2/3 power of its range, account being taken of the fact that ThC is complex. The activity of ThC found was in excellent agreement with that calculated for a multiple disintegration in which C_1 furnished 65 per cent. and C_2 35 per cent. as many α particles per second as the equilibrium amount of each of the other products of the thorium series, these being the percentages found in other ways by Marsden and Barratt[3] and Barratt.[4] The only discrepancy which appeared in the course of the work on thorium was traced to a large error in the accepted value for the range of ThX. But after the true range of ThX had been found, there was very good agreement between the observed activities and those calculated from the ranges of the various products. This led to the conclusion that there were no other α-ray products in that series than those already known; and that in each change, excepting that of the ThC, a single α particle is expelled from each exploding atom, while in the case of ThC the conclusions of Marsden and Barratt were fully confirmed.

In the present paper we wish to report the results of an analogous study of the actinium series, for which Table I. gives the latest available data.

We have prepared radioactinium (Rn) free from actinium itself as well as from actinium X, and subsequent products and measured its increase of alpha-ray activity with time, due to formation of AcX and its products. If f_1 is the fraction of the original Rn left after an interval of t days and f_2 is the fraction for AcX, unit amount being the equilibrium

[1] Geiger, Proc. Roy. Soc., *A*, *82*, 486 (1909). Taylor, Phil. Mag., *21*, 371 (1911). McCoy, PHYS. REV., *1*, 393 (1913).

[2] McCoy and Viol, Phil. Mag., *25*, 333 (1913).

[3] Proc. Lond. Phys. Soc., *24*, 50 (1912).

[4] Le Rad., *9*, 81 (1912).

quantity corresponding to the initial amount of Rn; then the activity, A, at time t, resulting from unit initial quantity of Rn is given by the equation:

$$A = f_1 + f_2 x, \qquad (1)$$

where x is the alpha-ray activity of the equilibrium quantity of AcX plus products for unit quantity of Rn. Strictly speaking, for intervals

TABLE I.

The Actinium Series.

	Symbols.	Periods.	Rays.	Ranges, Cm.
Actinium	Ac	?	—	—
Radioactinium	Rn	18.88 days[1]	$\alpha+\beta$	4.40[3]
Actinium X	AcX	11.35 days[2]	α	4.40
Emanation	Em	3.9 sec.	α	5.70
Actinium *A*	*A*	0.002 sec.	α	6.50
Actinium *B*	*B*	36 min.	β	—
Actinium *C*	*C*	2.1 min.	α	5.40
Actinium *D*	*D*	4.71 min.	$\beta+\gamma$	—

less than 3 or 4 days one should take into account the fact that the products of AcX are not in equilibrium with the latter; practically, however, for longer intervals, the simple equation (1) is entirely sufficient. If λ_1 and λ_2 are the decay constants of Rn and AcX respectively, then $f_1 = e^{-\lambda_1 t}$ and

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}).$$

The periods being 18.8 days and 11.35 days respectively, $\lambda_1 = 0.0369$ and $\lambda_2 = 0.0611$.

The actinium used in this work had been found to be free from all but negligible traces of radium and thorium and their active products.[4] It contained, however, an appreciable amount of ionium. To the solution of the actinium bearing material in dilute hydrochloric acid we added a few mg. of thorium nitrate and then precipitated the latter with hydrogen peroxide. The filtrate contained all the actinium and was apparently free from Rn and Io; but to be certain that no trace of the latter remained

[1] This paper.

[2] McCoy and Leman, Phys. Zeit., *14*, 1280 (1913). Hahn and Rothenbach found 11.6 days; Phys. Zeit., *14*, 409 (1913). The previously accepted periods of radioactinium and actinium X were 19.5 days and 10.2 days respectively.

[3] The range of radioactinium found by Geiger was 4.60 cm.; the value given above is that which we have found, as described in this paper.

[4] McCoy and Leman, loc. cit.

in the Ac, the treatment with Th and hydrogen peroxide was repeated three times. To the purified actinium solution 1 c.c. of 5 per cent. aluminium chloride solution was added and ammonia gas (free from carbon dioxide) passed in. The aluminium hydroxide was filtered out, dissolved in hydrochloric acid and precipitated with ammonia once more. The filtrate from the first aluminium precipitate contained two thirds of the AcX; that from the second the larger part of the balance; while 6 per cent. of the AcX remained in the third aluminium precipitate which contained practically all of the Ac. The precipitations with ammonia had freed the Ac from the minute amount of mesothorium introduced with the few milligrams of Th used. This Ac solution stood for several months during which time a large amount of Rn formed. The Rn was then separated from this solution, which had a volume of 5 c.c. by adding 3 drops of a 2 per cent. solution of thorium nitrate, which had just been freed from mesothorium, and precipitating the Th by hydrogen peroxide. The precipitate was filtered out, dissolved in dilute hydrochloric acid and potassium iodide, and precipitated by hydrogen peroxide four times more. The 10 c.c. of acid solution of the last Th precipitate which contained all the Rn but was entirely free from AcX and its products was treated with oxalic acid. The precipitate of 3 or 4 mg. of thorium oxalate contained all of the Rn. It was separated from the solution by a centrifuge, and washed thoroughly with water and then with alcohol. A small portion was then spread on a metal plate in an exceedingly thin film, the activity measurements of which are given in Table II.

TABLE II.

The Alpha-Ray Activity Curve of Radioactinium Initially Free from its Products. Film No. 4.

Interval in Days.	Activity.	x
0.000	1.000	
5.101	1.933	4.54
6.025	2.045	4.53
15.76	2.597	4.55
16.08	2.620	4.59
17.07	2.623	4.59
17.80	2.629	4.60
20.05	2.593	4.56
23.10	2.527	4.54
27.09	2.397	4.54
31.10	2.281	4.63
36.04	2.053	4.60
39.97	1.881	4.61
206.0	.007	4.573 mean

In the above table x is the activity of AcX + Em + A + B + C + D in terms of the activity of the equilibrium amount of Rn as unity.

The activity at the end of 206 days (Table II.) was found to be 0.007; of this 0.001 was calculated to be due to remaining Rn and products; the balance, 0.006, represents the constant activity of the minute amount of thorium present. The activities given in Table II. have been corrected for this constant thorium activity. The activity measurements were made in the alpha-ray electroscope previously described[1] having an ionization chamber 19.5 cm. square. The active films were placed 6.5 cm. below the charged electrode, thus allowing all rays to reach their full ranges. The activities of the films varied between half and one and one half that of the 35 sq. cm. standard film of uranium oxide. Sufficient potential, 500 to 600 volts, was used to insure practically complete saturation currents for the weak ionization measured.

Three other series of measurements like those represented by Table II. were made, with films made from two additional lots of radioactinium, each prepared and purified separately. The results for the four films are summarized in Table III.

TABLE III.

No. of Film.	No. of Observations.	x
1	18	4.59
2	14	4.57
3	15	4.55
4	12	4.57
		Mean 4.57

The value of x thus found is subject to a correction, which we estimate at 2.5 per cent., due to the effects of β rays, recoil, and loss of emanation. The corrected value is 4.68. By direct measurement we found that the β rays, largely from actinium D, increased the value of x 0.5 per cent. for the alpha-ray electroscope used in our measurements. To find the loss of activity due to recoil and loss of emanation we placed a brass plate charged to a negative potential of 110 volts one mm. above the radioactive film in a closed vessel and measured the activity which deposited on the plate during the first 16 days, following the preparation of the radioactinium film. Almost exactly half of the activity of the deposit was due to AcC; the balance decayed with the period of AcX, the presence of the latter substance being due to recoil. Assuming that all of the AcC lost by the film was deposited on the plate, the correction to x on this account would amount to 2 per cent. The correction for AcX, which is accompanied of course by Em and A, is also apparently 2 per cent., but should be taken somewhat less by reason of the probable

[1] McCoy and Ashman, Amer. Jour. Sci., *26*, 521 (1908).

extensive escape in the ionization chamber of the Em and A from the surface of the brass plate into the space above, where they would cause greater ionization than if they remained wholly on the plate. We estimate that the true correction should be 1.8 per cent. instead of 2 per cent. A further correction should be made because of the volatilization of Em and therefore of A from the principal film in the ionization chamber of the electroscope. From the amount of C in the active deposit, we estimate that 2 per cent. of the whole Em is present in gaseous form in the electroscope and that this would cause the value of x as found to be 0.8 per cent. too high. The combined effect of these corrections is $2 + 1.8 - 0.5 - 0.8 = 2.5$ per cent. Taking x uncorrected as 4.57, the corrected value becomes 4.68.

TABLE IV.

	Ranges at 15°.	$R^{\frac{2}{3}}$.	Percentage Activity.	
			Calculated.	Found.
Radioactinium	4.40	2.69	17.8	17.6
Actinium X	4.40	2.69	17.8	
Emanation	5.70	3.19	21.1	82.4
Actinium A	6.50	3.49	23.0	
Actinium C	5.40	3.08	20.3	
			100.0	

Table IV. shows the ranges, R, at 15° and 76 cm., $R^{\frac{2}{3}}$, and the percentage activity of each alpha-ray member of the series; these percentages are taken proportional to the corresponding values of $R^{\frac{2}{3}}$, it being assumed that the equilibrium amount of each member of the series produces the same number of alpha particles per second.[1] The values given in the last column of Table IV are those found by experiment: for radioactinium the "activity found" is $1/(1 + x) = 17.6$ per cent. of the whole. The value of $\Sigma R^{\frac{2}{3}}$ for AcX + Em + A + C divided by $R^{\frac{2}{3}}$ for Rn gives 4.63 which is therefore the theoretical value of x. The close agreement of this result with that found by experiment, 4.68, is further evidence, if such were necessary, that the roll of the alpha-ray members of the actinium series is now complete and that the constants given in Tables I. and IV. may be accepted with considerable confidence as being at least close approximates to the true values.

[1] While it is probable that AcC is complex, the number of α-particles of longer range than 5.4 cm. compared with those of this range is so small—0.15 per cent.—that we need not take them into account here. See Marsden and Perkins, Phil. Mag., *27*, 700 (1914).

Note One: The Period of Radioactinium.

Hahn's early work[1] on radioactinium indicated a period of 19.5 days. This value has been accepted during the past eight years and was thought to be confirmed by Rothenbach[2] during the past year, working under the direction of Professor Hahn. In determining the period of a radioactive substance, which produces products of considerably shorter life, it is usually practicable to consider that the rate of decay is exponential after a sufficient lapse of time. It was by this method of calculation that the period of radioactinium was determined by Hahn and by Rothenbach. However, in case the period of one or more of the products is of the same order of magnitude as that of the mother substance, this simple treatment of the problem is not accurate.

The familiar equation which we have used in the form

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

may be written

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} f_1[1 - e^{-(\lambda_2 - \lambda_1)t}] = \frac{p\lambda_2}{\lambda_2 - \lambda_1} f_1$$

if for $1 - e^{-(\lambda_2 - \lambda_1)t}$ we write p.

The equation

$$A = f_1 + f_2 x$$

then becomes

$$A = f_1 \left[1 + \frac{p\lambda_2 x}{\lambda_2 - \lambda_1}\right].$$

Now the limiting value of f_2 is given by

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} f_1$$

and to calculate the period of Rn by the simple exponential equation is to assume that f_2 has approached this limiting value sufficiently closely. But this is by no means the case, even after a much longer time than that over which Hahn's and Rothenbach's observations were carried. After 115 days the activity of a Rn film is about 6 per cent. less than it would be if the limiting ratio of AcX were present. Let us represent by A' the activity of the film if this limiting ratio of AcX (+ products) were present: then

$$A' = f_1 \left[1 + \frac{\lambda_2 x}{\lambda_2 - \lambda_1}\right]$$

[1] Phil. Mag., *12*, 244 (1906); *13*, 165 (1907).

[2] Dissertation, Berlin, 1913.

and

$$\frac{A'}{A} = \frac{\lambda_2 - \lambda_1 + \lambda_2 x}{\lambda_2 - \lambda_1 + p\lambda_2 x},$$

which expression we may call q, therefore $A' = qA$. It is obvious that the quantity A' will decrease with time strictly exponentially with the true period of Rn.

In order to find the period of Rn, we made a film from the larger part of the material used for the measurements recorded in Table II. This film had an initial activity nearly three times that of our uranium standard (about 35 sq. cm. of a thick film of U_3O_8). We made very careful measurements of its initial activity, extrapolating from the first measurements made 45 min. after the precipitation of the Rn with the thorium oxalate, to find the true activity at time zero. We allowed this film to decay for nearly four months and then made the measurements shown in Table V. between the 115th and 206th day, by which latter time the activity had fallen to 0.0469 of the uranium standard. Of this final activity we calculated that 0.0284 was due to the thorium present. We got this result by considering that of the activity observed at the 164th day, that due to Rn + products decayed exponentially with the period of 18.8 days, account being taken of the q factor. All of the observed activities given in Table IV. have been corrected for the constant activity of the thorium present. While a knowledge of the value of x is required for the calculation of q, any probable error in x is unimportant: thus, if x were 5.0 instead of 4.57, q would be changed by only 0.1 per cent. for the 115th day.

TABLE V.

Age of Film in Days.	Interval Since 115th Day.	Activity Found.	Activity Calculated.	q	Period of Radioactinium.
0.0	——	2.828			
115.1	0.00	0.4809	0.4804	1.060	——
117.1	2.02	0.4476	0.4473	1.058	18.94
127.9	12.02	0.3118	0.3129	1.045	18.68
132.0	16.91	0.2605	0.2630	1.040	18.60
139.1	24.00	0.2005	0.2032	1.033	18.56
145.9	30.82	0.1562	0.1592	1.028	18.59
152.9	37.80	0.1213	0.1238	1.024	18.67
160.0	44.89	0.0948	0.0954	1.020	18.84
164.1	49.01	0.0824	0.0823	1.018	18.97
206.0	90.87	0.0185	(0.0185)	1.007	(18.80)
				Mean Period found.....	18.74

From the consideration of all of our results on the change of activity of Rn films with time, we are led to conclude that the period of Rn is very

close to 18.8 days, although the results in Table V. lead to a mean of 18.74 days. We believe that better results for this constant would have been obtained if we had begun measurements before the activity of the film had become so small that the inevitable errors of measurement made appreciable errors in the period found. Using the value 18.8 days, we have calculated the activities to be expected from the activity, A_0, at time zero, by the strictly accurate equation

$$A = A_0(f_1 + f_2 x),$$

taking $A_0 = 2.828$ and $x = 4.57$. The results given in the column headed "Activity Calculated" were obtained in this way. It is seen that the agreement between these values and those found are quite as close as one could expect for films of such small activity. We have also made calculations of the activities at the various times upon the assumption that the period of Rn is 19.0 and 19.1 days. If the period of Rn is 19.1 days, the mean difference between the activities found and calculated is 5.9 per cent.; for a period of 19.0 days the difference is 3.7 per cent., while for a period of 18.8 days, the difference is only 0.8 per cent. It is therefore perfectly clear that the old value 19.5 days is far from the true value and can no longer be supported.

We find that the difference between our value for the period of radio-actinium and that of Hahn and Rothenbach is wholly due to the fact that in the latter case the formula used in the calculation was not sufficiently accurate. Our experimental results which are in satisfactory agreement with theirs, indicate also a period of 19.5 days, if we make the calculation by the simple exponential equation used by Hahn and Rothenbach. The latter's calculations were based on measurements made between the 115th and 174th day. Now a simple calculation will show that if the period as found by the simple exponential equation is 19.5 days for the interval between 120 and 139.5 days, then by use of the correct formula used by us, the same data show the true period to be 18.89 days.

Since the foregoing paragraphs were written we have completed four additional series of measurements of four new radio-actinium films and have obtained the results shown in Table VI.

TABLE VI.

Age of Film at First Measurement.	Age of Film at Last Measurement.	Number of Measurements.	Period.
60.1 days	109.2 days	11	18.88
60.1	118.0	12	18.88
104.0	120.0	7	18.75
92.2	119.2	6	18.88

The average difference between single results and the mean for the four series was 0.08 days. The low result, 18.75 days, for the third series was caused by three very low values found on successive measurements on the 9th, 12th and 14th days, viz: 18.56; 18.57; and 18.67. On both the 15th and 16th days, however, the measurements gave 18.84 days; and we are therefore inclined to think that these low results were caused by some undiscovered error in the activity measurement. If these low results are omitted from the mean, we obtain for this series 18.87 days, a value in good agreement with the means of the other three series.

These newer measurements indicate that the period of radioactinium is a little higher than 18.8 days, which value was used in finding the value $x = 4.68$. If, as is very probable, the period is 18.88 days, our experimental results give $x = 4.67$; the difference is not great and the lower value of x is in even closer agreement with the value calculated from the ranges, viz.: 4.63.

Note Two: Determination of the Range of Radioactinium.

The value found for the activity of the products of radioactinium compared with radioactinium itself led us to suspect either that the accepted range of radioactinium was too great or that of AcX too small. The values found by Geiger[1] for Rn and AcX at 15° and 760 mm. were 4.60 and 4.40 cm. respectively. Furthermore, by Geiger's law relating ranges and decay constants, the range of Rn should be less than that of AcX. As it was a comparatively easy matter to determine the range of Rn, we carried out this measurement, making use of a modification of Geiger's spherical flask apparatus. The flask, which was chosen from a large stock, was almost perfectly spherical, except in the region near the neck. Its internal radius was 6.7 cm.

The radiothorium was prepared by the same method as that used in preparing this substance for the activity measurements. A large quantity of actinium was used, and but one drop of a 0.4 per cent. thorium nitrate solution, = 0.1 mg. of ThO_2. The thorium was precipitated three times with hydrogen peroxide, and converted into oxalate, which was separated by means of a centrifuge and washed with dilute hydrochloric acid and finally with alcohol. A small portion of this oxalate was made into a very thin film, about 1 mm. in diameter on the center of the brass disc of the range apparatus. The range measurements were completed within two or three hours from the time of the oxalate precipitation; from which it follows that the maximum amount of AcX formed did not exceed 0.25 per cent. of the equilibrium amount. The

[1] Phil. Mag., *24*, 653 (1912).

temperature was read at frequent intervals during the measurement and always remained constant within one degree.

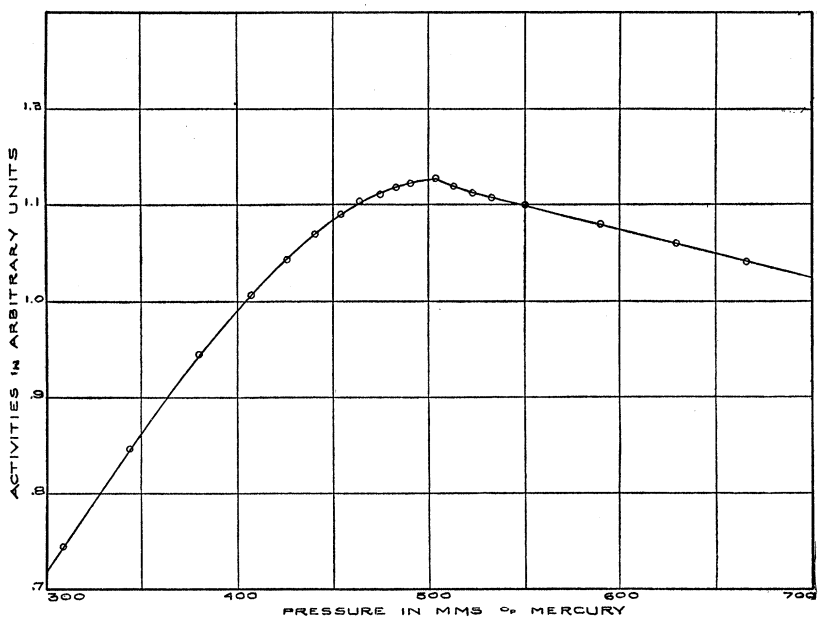

Fig. 1.

The results of one determination are shown graphically in Fig. 1, which is drawn to scale. The break comes at 504 mm. of mercury and as the temperature was 20°, this gives as the range of radioactinium 4.17 cm. at 760 mm. and 0°, or 4.40 cm. at 15°. We made two other determinations, each with separately prepared samples of radioactinium. One gave 4.38 cm., the other 4.43 cm. at 15°; the mean of the three results is 4.40 cm. for 15°. This is 0.20 cm. lower than Geiger found for radioactinium and is identical with Geiger's value of actinium *X*. The periods of radioactinium and actinium *X* being 18.8 and 11.35 days respectively, if the range of the former is 4.40 cm., that of the latter should by Geiger's law be 4.45 cm., which differs from the value found by Geiger by scarcely more than the experimental error of the measurements.

SUMMARY.

1. Methods are described for the chemical separation of radioactinium and also of actinium *X* from actinium and from one another and the preparation of each in radioactively pure form.

2. The period of radioactinium has been found to be 18.88 days instead of 19.5 days as accepted for many years. The old higher value resulted from an inaccurate method of calculation.

3. The period of actinium *X* has been found to be 11.35 days instead of 10.2 days. This result first published some months ago,[1] is in fair agreement with that found by Hahn and Rothenbach,[2] a few months earlier, viz.: 11.6 days.

4. The range of radioactinium at 15° and 76 cm. was found to be 4.40 cm. instead of 4.60 cm., as found by Geiger. The new value is in closer agreement than the old with Geiger's Law relating ranges and periods. This agreement is also improved by our results showing the period of radioactinium to be shorter and that of actinium *X* to be longer than the values formerly accepted. Complete agreement would result if the range of actinium *X* were 4.45 cm. instead of 4.40 cm. as given by Geiger.

5. Careful and extensive measurements of the change of the alpha ray activity of radioactinium with time has shown that the alpha activity of AcX + Em + A + C is 4.67 times that of the equilibrium amount of radioactinium alone. If in each atomic disintegration one and only one alpha ray is expelled, and if the ionization produced by any alpha ray is proportional to the 2/3 power of its range, we should expect this ratio to be 4.63. The good agreement between experiment and theory indicates the correctness of the latter. The important revised data for the actinium series are given in Tables I. and IV.

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[1] Phys. Zeitschr., *14*, 1280 (1913).
[2] *Ibid.*, *14*, 409 (1913).