

BULLETIN INTERNATIONAL  
DE L'ACADÉMIE DES SCIENCES DE CRACOVIE.  
CLASSE DES SCIENCES MATHÉMATIQUES ET NATURELLES.

N° 4.

Avril

1905.

Sommaire: 16. M. T. GODLEWSKI. L'actinium et ses produits.

Séance du lundi 3 Avril 1905.

PRÉSIDENCE DE M. N. CYBULSKI.

16. M. T. GODLEWSKI. *Aktyn i jego produkty. (Actinium and its successive products). (L'actinium et ses produits)*. Mémoire présenté par M. A. Witkowski m. t.

Rutherford and Soddy<sup>1)</sup> in their well known investigations on the activity of thorium have shown that it is possible to separate from it a very active constituent which they call ThX. The activity of this product decays with the time according to an exponential law i. e. the equation of monomolecular chemical reactions, falling to half value in about four days. At the same time, the thorium, which by the removal of thorium X, had been deprived of about 75% of its activity, recovered its activity, the recovery curve being complimentary to the curve of decay of ThX. The substance UrX, discovered earlier by Crookes, acts in a manner analogous to ThX. The activity of this substance decayed according to an exponential law, with the time falling to half value in 22 days.

Rutherford and Soddy have explained these phenomena on the supposition that the radioactive bodies are producing fresh radioactive matter at a constant rate and that the activity of the matter so formed decreases according to an exponential law with the time. The discovery of these phenomena supplied the basis for the disintegration theory which supposes that the atom of a radioactive body breaks up through a series of well marked stages. The

<sup>1)</sup> Rutherford and Soddy: Phil. Mag. Sep. and Nov. 1902. Trans. Chem. Soc. 81 321. and 807, (1902).



resulting products are quite distinct bodies, though they escape detection by chemical methods on account of the minute amount of the substance under investigation. Their existence is proved first of all by electrical measurements which allow us to make the quantitative investigations of the rate of change of these products.

On looking over the series of successive products arising from different radioactive bodies, striking similarity between the products of thorium and actinium is at once manifest. Thorium produces ThX, ThX the emanation, this gives rise to the active deposit which undergoes two further transformations, the first slow change being a rayless one, the other emitting all three kinds of rays. Actinium in like manner produces an emanation which is transformed into an active deposit which undergoes two further changes, the first being a slow rayless change and the other a rapid change.

This analogy in the number and nature of the products pointed <sup>1)</sup> to the possibility that there existed between the actinium and its emanation an intermediate product which bore the same relation to actinium that ThX bears to thorium. In a letter to Nature (26 Jan. 1905) I gave the preliminary results of the investigation which proved the existence of this product.

Taking into consideration the similarity of actinium and thorium, I applied to the actinium the same method which had been used by Rutherford and Soddy for the separation of ThX from thorium.

The experiments were made with the emanating substance of Giesel, which according to numerous investigations <sup>2)</sup>, has been found to contain the same radioactive constituent as the actinium of Debierne. The saturation current due to the  $\alpha$  ray activity of the products under investigations was measured with a quadrant electrometer of sensibility 120 divisions per volt; the needle was kept at the standard potential of 300 volts. The activity was measured by means of a sensitive electrocope. Four different sets of experiments were made which gave very concordant results.

In each case 0.15 g of the emanating substance, of activity

<sup>1)</sup> See: Rutherford: Bakerian Lecture: The Succession of Changes in Radioactive Bodies. Phil. Trans. of the Royal Soc. Ser A. 204 190 and 204.

<sup>2)</sup> See f. i. Rutherford. Bakerian Lecture Loc. cit. p. 188.

about 300 times that of uranium, was dissolved in 250 cm<sup>3</sup> of hydrochloric acid (about 8% concentration). The solution was evaporated on the water bath to about 100 ccm. When ammonia was added to the solution, a reddish-brown substance (probably hydroxide) was precipitated. The precipitate collected on a filter paper, was dried as quickly as possible and then its activity was measured. The filtrate was then evaporated to dryness, and when ammonium salts were driven off by ignition, a small amount of a brown black residuum was left behind on the dish. On raising this to a red heat the colour of the residue changed from black to white. This residue was intensely active compared with the weight. Immediately after the dish was cold the activity of the residue was measured and was found to decrease slowly with the time according to an exponential law. In the same period the actinium which by precipitation had been rendered almost inactive recovered its activity, the recovery curve being complimentary to the curve of decay.

From analogy to ThX, which so closely resembles in radioactive properties, the active substance separated from actinium will be termed Actinium X (AcX).

The results of one of the series of experiments are given in table I and graphically represented in Fig. 1. In table I the first column gives the days measured from the time of separation; the second column gives the activity. The activity of AcX is expressed as a percentage of the initial activity, the maximum activity soon after separation being taken 100. But for the actinium (deprived of AcX) the final value is taken 100.

Table I.

| <i>t</i> in days | Activity | <i>t</i> in days | Activity |
|------------------|----------|------------------|----------|
| 0.25             | 87.5     | 0.1              | 5.25     |
| 0.9              | 100      | 0.7              | 9.22     |
| 1.9              | 92.6     | 1.7              | 16.7     |
| 3.0              | 86.0     | 2.7              | 24.0     |
| 4.0              | 81.5     | 3.7              | 29.6     |
| 5.9              | 72.6     | 5.7              | 39.8     |
| 6.9              | 70.7     | 6.7              | 48.0     |
| 8.9              | 59.2     | 8.7              | 52.5     |

| $t$ in days | Activity | $t$ in days | Activity |
|-------------|----------|-------------|----------|
| 9.9         | 54.5     | 9.7         | 56.5     |
| 10.9        | 50.8     | 10.7        | 61.4     |
| 12.9        | 43.6     | 12.7        | 62.5     |
| 13.9        | 41.2     | 13.7        | 68.6     |
| 14.9        | 40.5     | 15.8        | 76.2     |
| 15.9        | 36.2     | 17.0        | 78.0     |
| 17.1        | 35.4     | 20.7        | 82.3     |
| 17.9        | 34.0     | 22.7        | 85.7     |
| 21.0        | 26.5     | 25.0        | 88.6     |
| 22.9        | 24.4     | 27.0        | 90.0     |
| 24.9        | 21.8     | 30.8        | 92.3     |
| 27.2        | 18.5     | 36.5        | 97.1     |
| 29.2        | 17.6     | 45.0        | 99.5     |
| 30.9        | 16.1     | 52.0        | 99.0     |
| 34.0        | 13.5     | 64.0        | 100      |
| 36.0        | 12.1     | 67.0        | 100      |
| 42.0        | 8.82     |             |          |
| 45.0        | 7.77     |             |          |
| 52.0        | 5.89     |             |          |
| 59.0        | 4.63     |             |          |
| 67.0        | 3.69     |             |          |

In Fig. 1 curve A represents the activity of AcX as a function of the time, the activity of AcX being expressed in the same units as in table I. In the recovery curve B the difference between the maximum and the first value is taken = 100.

The activity of AcX immediately after removal was weight for weight more than a hundred times as great as that of the original actinium. In the various experiments the value of initial activity of AcX was proportional to the amount of actinium used, but was by no means proportional to the total weight of matter obtained from the filtrate. In some cases, for example, only a few milligrams of the substance was obtained, which exhibited as great activity as a few centigrams obtained in other cases. This shows clearly that in case of actinium, the substance obtained from the filtrate, which we see and weigh, does not all consist of AcX. The substance contains some impurities; in the present case, probably some of the rare earths. The amount of actinium X actually

present is so minute that it precludes the possibility of a direct chemical investigation of its properties.

We see from table I that the activity of AcX increases in the first day after removal to about 15% of its original value,

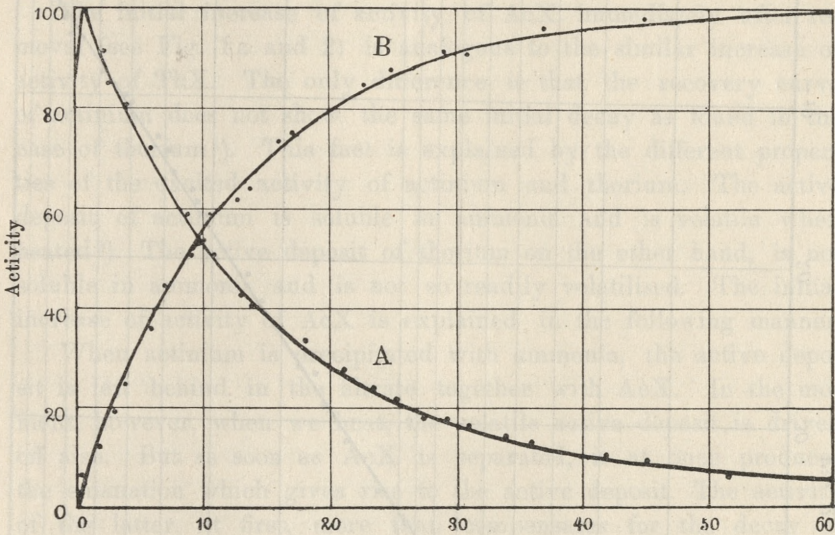


Fig. 1.  
Time in days.

reaches a maximum, and then decays with the time according to an exponential law falling to half value in 10.2 days. This exponential law of decay is clearly seen in Fig. 2, where the ordinates represent the logarithms of the activity of the product AcX, and the abscissae the time after separation. On subtracting from the quantities given in the table I the number 2.70, which represents the activity of the residue which did not decay with the time the points fall accurately on a straight line as in the figure. This non decaying residue comes probably from the small amount of actinium, which is not precipitated and is therefore present in the filtrate.

The activity of actinium, from which actinium X was removed, increased so that the recovery curve was approximately complimentary to the decay curve of AcX. The small difference between the experimental and the theoretical curve, as expressed by the

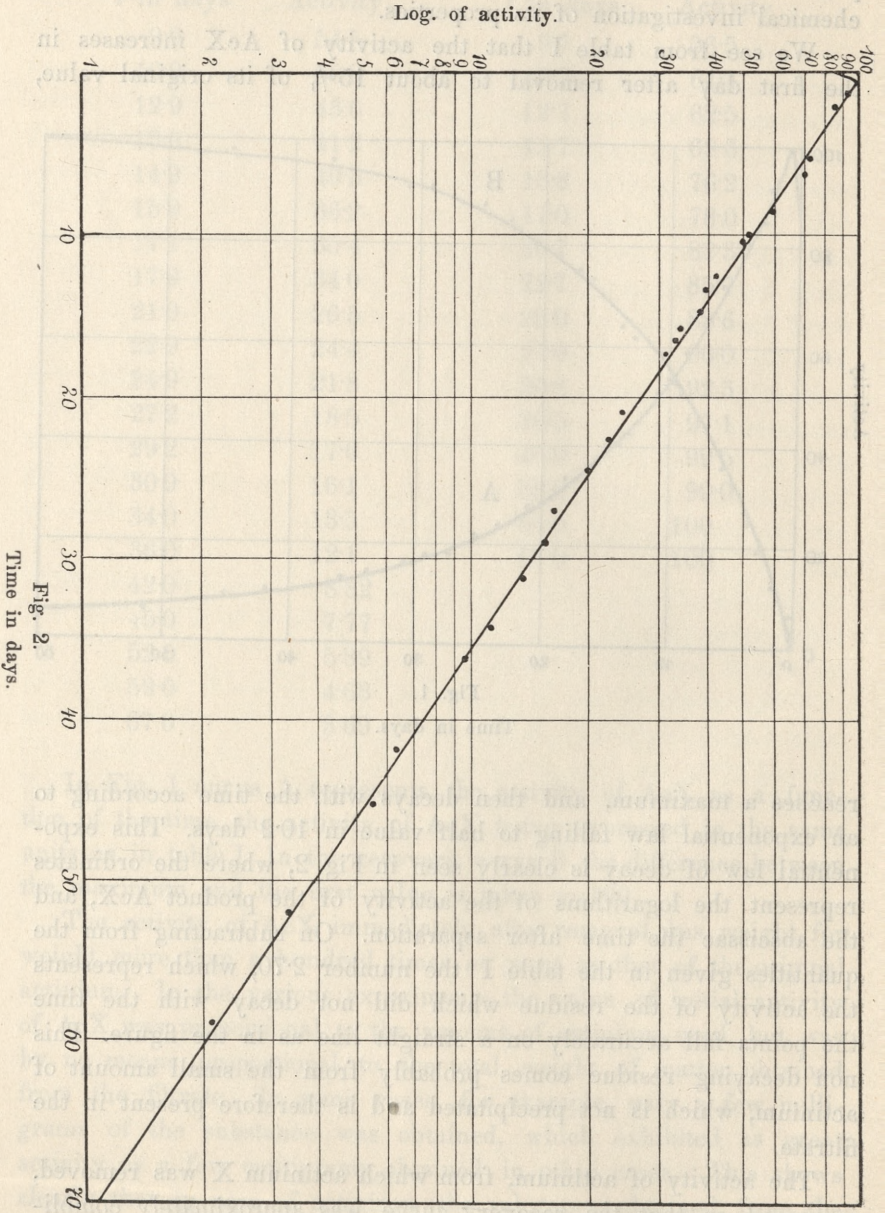


Fig. 2.

equation  $I = I_0 (1 - e^{-\lambda t})$ , where  $\lambda$  has the same value as in the decay curve, is probably due to a variation in the rate of escape of the excited activity, which is extremely volatile. In all cases the decay curve agreed more closely with the theoretical equation than the recovery curve.

The initial increase of activity of AcX immediately after removal (see Fig. 1 a and 2) is analogous to the similar increase of activity of ThX. The only difference is that the recovery curve of actinium does not show the same initial decay as found in the case of thorium<sup>1</sup>). This fact is explained by the different properties of the excited activity of actinium and thorium. The active deposit of actinium is soluble in ammonia and is volatile when heated<sup>2</sup>). The active deposit of thorium on the other hand, is not soluble in ammonia and is not so readily volatilised. The initial increase of activity of AcX is explained in the following manner.

When actinium is precipitated with ammonia, the active deposit is left behind in the filtrate together with AcX. In the moment, however, when we heat, the volatile active deposit is driven off also. But as soon as AcX is separated, it at once produces the emanation which gives rise to the active deposit. The activity of the latter, at first, more than compensates for the decay of activity of AcX, which has a comparatively slow change, and in consequence the activity of AcX first of all increases.

On the other hand, the actinium, when treated with ammonia was deprived not only of AcX but also of most of the active deposit. Any of the latter if still remaining in the precipitate, would be driven off during the process of drying. In consequence, when we start the measurements of the activity of the precipitate itself, no excited activity is present. The activity at once commences to increase since a fresh amount of AcX is produced which in turn gives rise to excited activity. In consequence we do not observe the initial decay in the recovery curve of actinium as in the corresponding curve for thorium.

Disregarding these small peculiarities, the behaviour of the

<sup>1</sup>) See Rutherford: Radioactivity p. 180 and 295.

<sup>2</sup>) The more complete account of the physical and chemical properties of the active deposit of actinium will be published later as the experiments are not yet completed.

product AcX, and of actinium deprived of AcX, is, as we have seen, completely analogous to that of ThX and of thorium deprived of ThX. There is however the following distinct difference. After removal of ThX, thorium always has a certain amount of residual activity about 25% of maximum value. A similar effect is observed in the case of radium, where the „de-emanated“ radium has always a non separable activity of about the same (25%) value. In the case of actinium, immediately after removal of AcX, the actinium is almost inactive, its activity being only 5% of its maximum value. I tried experiments to see if this activity could not be removed by means of successive precipitations with ammonia, but although 8 precipitations were made in the course of 7 hours the residual activity always remained. Nevertheless, the smallness of the initial amount of activity pointed to the probability that in reality the actinium itself is not active and that the residual activity observed is due to a small quantity of AcX, which is left behind. The interval between the last precipitation and the first measurement was always one hour or more, but this alone would not account for the observed current. It seems very probable that at the moment of the removal of AcX, if the separation were complete, actinium would be entirely devoid of activity. From the point of view of the theory of radioactive changes, this shows that the change of actinium into AcX is not accompanied by either  $\alpha$ ,  $\beta$  or  $\gamma$  rays or, in other words, is a „rayless“ change.

By means of an electroscope, it was found that actinium X gave out all three kinds of rays  $\alpha$ ,  $\beta$  and  $\gamma$ . Now the products of excited activity are very quickly formed owing to the very rapid change of the emanation. The activity of these products are consequently measured together with AcX. It was separately proved that the active deposit gave out  $\beta$  rays<sup>1)</sup>. Taking into consideration the analogy with thorium and even with radium, we should expect that the measured  $\beta$  activity of AcX arises not from AcX itself, but from the excited activity resulting from it. There is however strong evidence that in the case of actinium the  $\beta$  and

<sup>1)</sup> It was found that the excited activity of actinium, measured by  $\beta$  rays, after a long exposure decayed according to an exponential law with the time, falling to half value in 36 minutes. The complete account of these investigation will be given in another place.



probably the  $\gamma$  rays are emitted also by AcX itself. For instance, the curves of decay of activity of AcX measured by  $\alpha$  and  $\beta$  rays are throughout identical even from their beginning; and further, the activity of AcX measured by  $\beta$  rays, 5 minutes after strong heating, when all the volatile excited activity should be driven off, exhibits a very great initial value, which could not be the case if the  $\beta$  rays were emitted only by excited activity.

It is thus most probable that AcX itself gives rise to all three kinds of rays.

### Source of the actinium emanation.

In the case of thorium the product ThX was intermediate between thorium and its emanation. In order to see if AcX occupies the same position in actinium, I measured the rate of change with time both of the emanating power of AcX and of actinium from which AcX was removed. The measurements of activity of the emanation were made in a cylindrical brass testing vessel<sup>1)</sup> in the interior of which three insulated electrodes were placed; during the measurements one of the electrodes was connected with an electrometer and the other two were earthed.

Both actinium X and actinium deprived of AcX were placed in solutions of ammonium chloride in two bubbling flasks, and these could be successively connected with the testing cylinder in which the amount of emanation was measured. For the purpose of comparison with a substance of a standard emanating power the following arrangement was used.

The current of air passed through the bubbling bottle and carried with it the emanation of the product to be investigated. It thus passed through the testing cylinder in which the activity of the emanation was measured. On leaving the cylinder the current of air entered a glass tube 2 cms in diameter and about 2 meters long. At the end of this glass tube some fresh solid actinium was placed and the emanation from this was carried into the second testing cylinder where its activity was measured.

In this manner the same current which carried the emanation from the product under investigation, also carried the emanation from the standard actinium. In passing through the long and wide

<sup>1)</sup> See Rutherford: Radioactivity p. 199 and Fig. 37.

glass tube the emanation which left the first cylinder decayed completely before reaching the second cylinder. By this method of measurement the emanating power of AcX was directly compared with the standard emanating power of solid actinium.

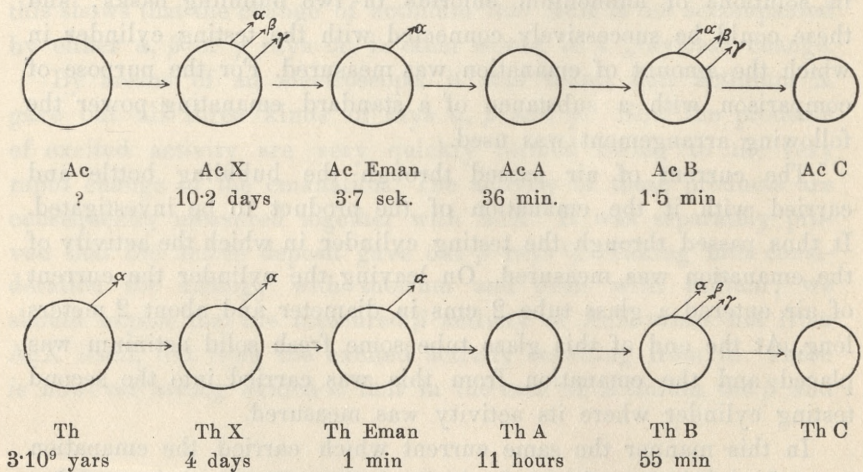
The experiments made in this manner showed:

- 1) That the actinium immediately after removal of AcX gives practically no emanation.
- 2) That the rate of increase of the emission of emanation of actinium after removal of AcX is the same as the rate of increase of its activity.
- 3) That the emanating power of AcX decreases at the same rate as the activity of AcX.

Since the emanation is only observed when actinium X is present and is always proportional to the amount of actinium X, it must be a product of actinium X.

The changes occurring in actinium are shown in the following graphical representation<sup>1)</sup> together with the period required for transformation to half value. For comparison the changes taking place in thorium are also given.

Table 2.



<sup>1)</sup> See Rutherford Bakerian Lecture Loc. cit. pp. 180—190 and 204; also Miss Brookes Phil. Mag. Sept. pp. 382—384; (1904) also Bronson Amer. Journ. of Science Vol. XIX, Feb. pp. 187. (1905).

It is seen that there is a very striking similarity between the number and nature of the changes for actinium and thorium. But the periods of decay, the radioactive, chemical and physical properties of the products of actinium all point conclusively to the fact that we have in actinium a distinct chemical element.

Whilst writing this paper the December number of the „Jahrbuch der Radioaktivität und Elektronik“ was received containing a paper by Giesel on emanium<sup>1)</sup>. In this paper Dr. Giesel gives an account of his investigation, in which he finds that it is possible to separate from emanium by precipitation with ammonia a small amount of very strongly active substance. The method of separation employed by him was then identical with the method I have used. I cannot, however, compare quantitatively my results with his, inasmuch as Dr. Giesel does not publish any measurements.

A short account will now be given of some experiments which are still in progress on the nature of the  $\beta$  and  $\gamma$  rays of actinium.

The  $\beta$  rays of actinium are completely distinct in their character from the  $\beta$  rays emitted by the other radio-elements, inasmuch as they are completely homogenous. This fact was established by the measurements of absorption of  $\beta$  rays in passing through solid bodies. The activity measured by  $\beta$  rays decreased strictly according to an exponential law with the thickness of matter traversed. The equation  $I = I_0 e^{-\lambda d}$  where  $d$  is the thickness was applicable even in the case when  $I$  was less than 1% of its original value.

The  $\beta$  rays from actinium differ also from the  $\beta$  rays of other radioactive elements in the absolute value of the absorption constant  $\lambda$  which is about 2.5 times as great with actinium as with uranium. Thus the  $\beta$  rays of actinium have less than half the penetrating power of those emitted by any other radio-element.

The existence of the  $\gamma$  rays from actinium was also distinctly proved. The absorption measurements showed that the  $\gamma$  rays of actinium are fairly homogenous and their penetrating power was only about one quarter of that observed for the  $\gamma$  rays from radium. A more complete account of these investigations will be published later on.

<sup>1)</sup> Giesel: Untersuchungen über das Emanium (Actinium) Jahrbuch f. Radioakt. VI. pp. 375—358.

In conclusion it is my most pleasant duty to express my deepest gratitude to Prof. Rutherford for suggesting these investigations, for his kindness in the advice he has so freely given to me and for placing at my disposal all the plentiful resources of his laboratory at McGill University.

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Nakładem Akademii Umiejętności.

Pod redakcją

Członka delegowanego Wydziału matem.-przyr., Dra Leona Marchlewskiego.

Kraków, 1905. — Drukarnia Uniwersytetu Jagiellońskiego, pod zarządem J. Filipowskiego.

3 Maja 1905.

